# DEVELOPMENT OF PLASTIC HEAT EXCHANGERS FOR OCEAN THERMAL ENERGY CONVERSION

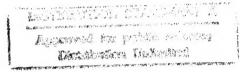
Final Report for August 1976-December 1978

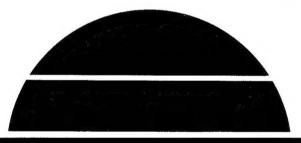
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January 1979

Work Performed Under Contract No. EY-76-C-05-5165

DSS Engineers, Inc. Ft. Lauderdale, Florida





# **U.S.** Department of Energy

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Solar Energy

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FOR

OCEAN THERMAL ENERGY CONVERSION

FINAL REPORT

August, 1976 - December, 1978

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January, 1979

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PREPARED FOR THE

U. S. DEPARTMENT OF ENERGY

SOLAR ENERGY

UNDER CONTRACT EY-76-C-05-5165

PETQUATE STORY

#### **EXECUTIVE SUMMARY**

Extensive work in the field of sea water desalination, including some plastics applications, suggested to DSS Engineers, Inc., in 1973, that plastics might have a significant cost advantage over corrosion resistant metal alloys for some low temperature marine heat transfer applications. The enormous amounts of heat transfer surface required by the closed cycle Ocean Thermal Energy Conversion (OTEC) process made it a likely application to consider. DSS Engineers was awarded a grant in May 1974 by the RANN Directorate of the National Science Foundation to make a design study and cost estimate of plastic heat exchangers (PHX) for OTEC. The results of this initial feasibility study indicated that plastic heat exchangers were technically feasible and economically attractive, but that several technical areas of uncertainty existed. In August, 1976 a two-year materials testing and evaluation program was begun by DSS Engineers for DOE. Its primary objective was to make material selections and answer the most important technical questions raised by the previous feasibility study.

To select potential core material resins for the test program, a review of thermoplastic properties and applications was made. A cost parameter based on the cost estimates of the initial feasibility study was developed to compare the merits of various commercially available plastics. In addition, chemical resistance indicators including solubility parameters, dielectric constant and manufacturers' application recommendations, were examined to determine probable compatibility with sea water and the three proposed working fluids, ammonia, propane and isobutane. Seven plastics representing a fairly broad spectrum of polymer families were selected for experimental screening. They are: high density polyethylene (HDPE), polypropylene, polybutylene, polyvinylchloride, acetal copolymer, nylon II and cellulose acetate butyrate.

The simplicity of chemical resistance tests allowed a large number of environment/material combinations to be performed in a relatively short time. Specimens of the seven plastics were exposed independently to air, sea water, liquid ammonia, liquid isobutane and liquid propane for a period of seven days at 80 F. Changes in tensile properties, weight and dimensions were measured. The main purpose of these tests was to screen the least suitable materials from the development program rather than to produce information directly applicable to heat exchanger design. All seven plastics exhibited good resistance to sea water, nylon, PVC and acetal were resistant to isobutane and propane; HDPE, polypropylene, polybutylene and acetal were resistant to ammonia.

In the interests of campatibility with the overall OTEC program, experimental work subsequent to the chemical resistance tests was oriented toward ammonia resistant plastics. HDPE, polybutylene and acetal were chosen for environmental rupture constant tensile loads in these environments to determine: 1) dependence of tensile failure stress on time and environment; 2) susceptibility to environmental stress cracking; 3) creep extension under constant load. The load bearing ability of HDPE was essentially unaffected by sea water or ammonia. Ammonia caused pronounced reductions in failure stresses of acetal and polybutylene. The minimum projected tensile stresses to produce failure at 100,000 hours for HDPE, polybutylene and acetal are, respectively, 1057, 1585 and 2115 psi. Environmental stress cracking was not observed in any of the tests.

Based on the results of the environmental rupture tests, high thermal conductivity, low price and proven suitability for complex extrusions, HDPE was chosen for long term durability testing. Sections of extruded "plate tube" panels exposed to simulated OTEC environment for periods in excess of 3000 hours confirmed that HDPE will perform reliably at predicted stress levels.

To explore enhancement of thermal conductivity, HDPE was compounded with 10% and 15% by weight acetylene black filler. The thermal conductivities of these compounds were measured and compared with unfilled HDPE. Results indicated that theremal conductivity may be increased by 50% with a 34% filler loading. Tensile and environmental rupture tests of filled HDPE shows improvement in mechanical properties over the unfilled plastic.

Since plastics are low density material in consequence of their relatively loose structure, they are not an absolute barrier to the transmission of ammonia. The transmission rates for ammonia liquid and vapor and their temperature dependence were determined experimentally for HDPE. Saturated ammonia liquid permeates about twice as fast as the saturated vapor at the same temperature. To find a permeation barrier effective against ammonia, several materials and surface treatments were tested. Sulfonation, a gas phase surface treatment for HDPE, was found to be a moderately effective ammonia barrier. Ammonia loss for a double-side sulfonation treated 10 mil thick HDPE wall would be reduced by 86 % as compared to an untreated surface.

A review of the mechanisms of biofouling indicated that the settlement and subsequent colonization of bacteria appears to be a necessary prerequisite for biofouling of a plastic surface placed in contact with sea water. Conventional methods for preventing or controlling biofouling were revealed to be either too costly or ineffective in controlling this primary fill formation. Subsequent investigations into alternative means of preventing or controlling film formation on plastic heat exchanger surfaces indicated that the bacterial process of negative chemotaxis offers real possibilities for achieving this. The semi-permeable nature of the plastic heat exchangers presents several possible mechanisms for bringing a bioinhibiting compound to the seawater surface of the heat exchanger. Three of the most promising mechanisms are: 1) incorporating the repellent into the resin backbone; 2) permeation of the repellent through the heat exchanger; selective absorption of the repellent into the heat exchanger with subsequent slow release into the sea water-heat exchanger interface. Tests by other investigators of the ability of several organic compounds to initiate negative chemotaxic responses indicate that benzoic acid is the most effective one.

The design of a plate-type ammonia condenser core test unit was added as a parallel development effort to the material testing program by contract modification in 1977. A detailed thermal and mechanical design for a 900,000 Btu/hr duty condenser compatible with the Argonne heat exchanger test facility was completed. The first fabrication step, extrusion of 4' x 10' "plate-tube" HDPE panels, was successfully completed. Techniques for producing the critical joints at the panel bundle headers were extensively explored. Electromagnetic induction welding was identified as the best state-of-the-art process.

It is <u>recommended</u> that work continue by 1) fabricating and testing for heat transfer capability, a prototype condenser; 2) develop up-to-date technical and economic aspects of application and; 3) experimentally determine further improvements possible in reducing ammonia transmission, increasing thermal conductivity and creating a non-fouling surface.

## FOR

# OCEAN THERMAL ENERGY CONVERSION

# FINAL REPORT

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#### **ABSTRACT**

[Materials and processes have been selected and design information was obtained for plastic ocean thermal energy conversion (OTEC) heat exchangers as the result of a program comprising five types of laboratory experiments. Tests to evaluate the chemical resistance of seven commercially available thermoplastics to sea water and several possible working fluids were conducted with emphasis placed on compatibility with ammonia. Environmental rupture tests involving exposure of stressed specimens to sea water or liquid ammonia indicated that the high density polyethylene (HDPE) is the best suited candidate and produced an extrapolated 100,000 hour failure stress of 1060 psi for HDPE. Long term durability tests of extruded HDPE plate-tube panel confirmed that plastic heat transfer surface is mechanically reliable in an OTEC environment. Thermal conductivity measurements of acetylene black filled HDPE indicated that conductivity may be increased by 50% with a 35% by weight filler loading. The permeability coefficient measured for liquid ammonia through HDPE was higher than previous estimates. Test showed that the rate can be significantly reduced by sulfonation of HDPE. A review of biofouling mechanisms revealed that the permeable nature of the plastic heat exchanger surface may be used to control primary biofouling form formation by allowing incorporation of non-toxic organic repellents into the plastic. A preliminary design and fabrication development program suggests that construction of an ammonia condenser test unit is feasible using currently available materials and manufacturing techniques.

#### SECTION 1

#### INTRODUCTION

## 1.1 PURPOSE AND OBJECTIVES

The purpose of this program is to demonstrate the technical feasibility of utilizing plastic heat exchangers (PHX) in closed cycle ocean thermal energy conversion (OTEC) systems by qualifying a commercially available thermoplastic for this service.

Specific objectives are as follows:

- Select materials compatible with sea water and potential OTEC working fluids.
- 2. Determine the long-term strength and service life in an OTEC environment.
- 3. Determine the thermal conductivity of plastic incorporating thermally conductive filler material.
- 4. Determine the permeability of the heat transfer surface to working fluid and identify means of reducing permeability if necessary.
- 5. Explore the anti-fouling potential of plastic through polymer modification or additive incorporation.
- 6. Design an ammonia condenser test unit to explore mechanical integrity, fabrication techniques and thermal performance.

#### 1.2 BACKGROUND

Ocean thermal energy resources, although enormous and renewable, can only be converted to useful work with low thermal efficiencies because of the small temperature differences involved. About 40 times more energy must be added to an OTEC system than is extracted as net work and an almost equally large amount of energy must be rejected. Heat exchangers for a system utilizing a secondary working fluid will consequently be huge and costly.

Most efforts to date aimed at improving cost effectiveness of OTEC heat exchangers have concentrated on improving heat transfer coefficients through the use of modified heat transfer surfaces. Another approach is to reduce the cost per unit area of heat transfer surface by simplifying construction and/or utilizing less expensive materials. This second approach was taken by DSS Engineers in a previous study of the feasibility of utilizing plastic heat transfer surfaces for OTEC heat exchangers.

Although plastics are seldom employed as heat transfer surfaces, a number of experimental and commercial heat transfer applications have been developed. Table 1-1 lists some of these. The unique nature of closed cycle OTEC plants is such that plastics may constitute a viable, low cost alternative to metal alloys. Advantages over the alloys conventionally employed in marine heat exchangers are: 1) low material cost;

abundance of material supply;
 relative ease of manufacture; and
 immunity to electrochemical attack. Major disadvantages include:

low thermal conductivity;
 low long term strength;
 and 3) high permeability of contact fluids.

This report describes an experimental program conducted to evaluate selected commercial thermoplastics for this service and provide preliminary data for heat exchanger design. Five types of experiments were 1) chemical resistance; 2) environmental (creep) rupture; 3) thermal conductivity; 4) working fluid permeability; and 5) long-term durability.

In addition to materials testing tasks, this PHX development program included as a parallel effort the design and fabrication of a core test unit. This unit is an ammonia condenser of plate-type configuration. Design and fabrication methods are covered in this report.

All materials tests described in this report were performed at the Florida Atlantic University Marine Materials and Corrosion Laboratory.

#### 1.3 CONCLUSIONS

The results of this program strengthen the major conclusion of the previous report which states that application of the PHX in an OTEC system is technically feasible. The following specific conclusions support this statement.

- 1) HDPE has been proven a qualified material for a PHX in an OTEC system using ammonia working fluid. This is primarily because of its combination of (relatively) good thermal conductivity and long-term strength in the OTEC environment.
- 2) The thermal conductivity of HDPE may be improved 50% by compounding the HDPE with 34% by weight acetylene black. However, other filler materials would probably enhance conductivity more effectively.
- 3) Acetylene black filled HDPE exhibits satisfactory chemical resistance and creep behavior in ammonia and sea water.
- 4) A significant reduction of the rate of ammonia transmission through HDPE can be achieved by sulfonation of the heat transfer surface.
- 5) Large HDPE "plate-tube" panels have been extruded successfully. Short term burst tests and long term durability test of the panel in a simulated OTEC environment have shown no reduction in material strength caused by processing or environment.
- 6) For assembly of large PHX bundles, electromagnetic induction welding appears to be the most promising technique.
- 7) Fabrication of an ammonia condenser test unit is feasible using currently available materials and manufacturing processes.

#### 1.4 RECOMMENDATIONS

Based on the results of this study, the following recommendations are made in order to pursue the PHX development already undertaken to its logical conclusions to enable the DOE and other OTEC investigators to objectively assess the overall future of PHX in the OTEC program.

These recommendations are as follows:

- Determine the up-to-date technical and economic aspects of utilizing the PHX in OTEC plants. This would involve making conceptual designs of full-size heat exchangers in sufficient detail to estimate costs and thermal performance.
- 2) Demonstrate fabricability and thermal performance of a PHX by building and testing a condenser core test unit.
- 3) Determine the effectiveness of fluorinating HDPE to reduce the rate of ammonia transmission. This treatment appears as promising as sulfonation.
- 4) Explore the potential of one or two other filler systems for enhancing the thermal conductivity of HDPE.
- 5) Evaluate the possibility of calcareous deposit formation on the sea water side of a plastic surface caused by ammonia permeation.
- 6) Experimentally evaluate the possibility of creating a non-fouling plastic heat transfer surface through the use of organic repellents.

Table 1-1

Heat Transfer Surface Applications

of Plastic Materials

<u>Application</u>	Country	Material
MSF sea water distillation	U.S.A.	polyvinylfluoride, XL poly- ethylene
MSF sea water distillation	U.K.	polyethylene, polypropylene, polycarbonate
MSF sea water distillation	Israel	polypropylene
Chemical process	U.S.A.	polytetrafluoroethylene
Solar collectors	U.S.A.	polypropylene, XL polyethy- lene
Snow melting	U.S.A.	polybutylene
Air heat recovery	U.S.A.	polyamide
Dry cooling tower	Italy	polyethylene

#### SECTION 2

#### MATERIALS SELECTION STUDIES

#### 2.1 COST OF HEAT TRANSFER SURFACE

Our approach in the previous study was to concentrate on the largest family of commercial polymers, the thermoplastics, in order to take advantage of their low cost, ease of processing and suitability for temperatures encountered in the OTEC application. To meet the specific requirements of an OTEC plant a multi-component plastic heat transfer surface was proposed that would consist of core material, conductive filler and barrier layer(s).

The core material is the plastic resin that acts as a matrix for the conductive filler particles and forms the basic shape of the heat transfer surface. Its primary function is to provide the strength required to withstand pressure differentials imposed by heat exchanger operating conditions. This component should also have high thermal conductivity since it forms the major part of the wall's thermal resistance.

The concept of cost per unit property has been proposed as a means of evaluating various materials for a particular application. When only one physical property is of interest, this approach provides a simple means of comparison. In the present case, however, at least three physical characteristics and resin price must be taken into consideration. The conceptual designs in previous report provide a relative estimate of the cost components for production of plastic heat transfer surface for a particular heat transfer duty and the sensitivity of these costs to variations in material properties.

A simple cost factor was derived from the compact heat exchanger cost estimate in that study and used to compare various plastics to the reference material, high density polyethylene (HDPE). The cost of producing heat transfer surface from bulk materials through assembly of "modules" ready for installation in a heat exchanger depends roughly on material volume term and two heat transfer area terms according to the following expression:

ion; 
$$\frac{NAN\$}{NS} = 4.31 \frac{NA}{E} + 4.54 NA$$
  
F\\$ =  $\frac{NS}{9.85}$  (2-1)

where

NA = area parameter,

No = strength parameter, T/T HDPE

N\$ = cost parameter,  $S_G \times \frac{1b}{b} / (S_G \times \frac{1b}{b} + DPE)$ 

E = ease of extrusion factor (from 1.0 to 0.5)

t = wall thickness,  $8.3 \times 10^{-4}$  ft/No

 $k = thermal conductivity, Btu/hr - ft^2 - F$ 

T = short term tensile strength

S<sub>G</sub> = specific gravity of resin

The cost factor, F\$, for each material is an indicator of how expensive it might be, relative to HDPE, to produce modules in that material for an equivalent heat transfer duty.

Table 2-1 summarizes material properties and cost factors for a number of commercial plastics. The above expression is based on numerous simplifications; one of the more significant is the use of readily available short term tensile strength data rather than long term strength. Were it available for all plastics listed in Table 2-1, the Plastic Pipe Institute's Hydrostatic Design Basis would be a suitable long term tensile strength figure for comparison purposes. As expected, HDPE compares very favorably with other plastics. The most interesting result is that a large number of materials might be economically attractive for this application even though many of them cost several times as much as HDPE on a per pound basis. Raw material costs are overwhelmed by the area dependent fabrication costs and only become significant for extremely expensive materials like the fluoroplastics. It should be noted that the cost per pound figures in Table 2-1 are for 1976. They have not been updated since they are presented for comparison purposes only. Chemical resistance to specific environments and other factors affecting the long term life expectancy of individual plastics were not considered in the above comparison. These are discussed in the following sections.

## 2.2 CHEMICAL RESISTANCE INDICATORS

The term "chemical resistance" is commonly used to refer to many facets of the behavior of plastics in chemical environments. In this instance we are primarily concerned with the effects of immersion in sea water and OTEC working fluids on mechanical properties. The following three working fluid candidates were considered in this program: anhydrous armonia, propane and isobutane. Ammonia and propane are the two fluids that have received the most attention from OTEC investigators. Isobate ane although not as thermodynamically attractive, might be advantageous for a system using plastic heat exchangers principally because of its lower vapor pressure at corresponding temperatures.

As indicated in the previous section, a large number of plastics might be suitable for this application. To avoid testing all of them, several chemical resistance indicators were examined to try to avoid obvious incompatibilities.

#### Solubility Parameters and Dielectric Constants

The effects of a chemical environment on a plastic may be caused by either physical or chemical interaction. Chemical effects involve some type of molecular change such as oxidation, cross-linking or reduction in molecular weight. Perhaps more commonly encountered are physical or solubility effects. A liquid will be a solvent for another material if the molecules of the two materials are compatible; they must be able to co-exist on a molecular scale without tending to separate. Co-existence will be possible if the force of attraction between different molecules is not less than the forces of attraction between like molecules of either species. These forces can be expressed quantitatively through a

Table 2-1

# Cost Factor Comparison

	TENSILE STRENGTH psi	THERMAL CONDUCTIVITY Btu/Hr ft² - F	COST/ POUND	SPECIFIC GRAVITY	EASE OF EXTRUSION FACTOR	COST FACTOR
	11,500	.140	\$ .84	1.14	_	1.0
	10,900	.140	.84	1.13	_	0.
High Density Polyethylene	4,300	. 283	. 29	0.95		1.0
•	10,000	.133	.73	1.42	<b>_</b>	1.0
	000,6	.121	.57	1.19		
Acrylonitrile Butadiene-Styrene	5,250	.151	.49	1.04	<del></del>	1.2
te	6,250	.145	.73	1.30		1,3
	8,000	.126	1.37	1.04	<b>,</b> —	1,3
	7,800	.126	1.34	1.08		 
	8,750	111.	.92	1.20	ထ့	۳.
Polyester Thermoplastic	8,200	.134	1.47	1.35		<del>.</del> 3
	4,800	.125	.60	0.93	_	1.4
te Butyrate	4,750	.145	.77	1.19	_	 5
Styrene-Acrylonitrile-Copolymer	10,500	.070	.40	1.09	9.	1.5
Medium Density Polyethylene	2,350	.218	2.85	0.93		ر م
Polypropylene Homopolymer	4,900	.068	.27	0.91		1.7
Polyvinylchloride	6,750	.103	. 34	1.44	٠,	∞ <u>.</u>
	2,000	.131	1.70	1.13	_	9.0
Low Density Polyethylene	1,450	194	. 28	0.92	_	2.3
	4,250	.048	.29	1.07	_	2.5
Chlorotrifluoroethylene	7,000	.092	8.24	1.68	<b></b>	5.1
Tetrafluoroethylene	3,500	.145	4.62	2.17	n.	ထ

parameter known as the "cohesive energy density" or the energy of vaporization ,  $\Delta E$ , per molar volume,  $V_m$ , i.e.

$$\frac{\Delta E}{V_{\rm m}} = \frac{L - RT}{M/D} \tag{2-2}$$

where L is the latent heat of vaporization, R is the gas constant, T is the absolute temperature, M is the molecular weight and D is the density. More commonly encountered is the square root of the cohesive energy density which is known as the solubility parameter.

For amorphous non-polar polymers and amorphous non-polar solvents, solvation can only occur when the polymer and the solvent have similar solubility parameters. Experience has indicated that the range must usually be within  $2x10^2 \, (J/M^3)^2$  for solvation to occur.

In the case of crystalline non-polar polymers and/or solvents, the process of crystallization results in a decrease in free energy and in order for the process to reverse (for melting to occur) additional energy must be introduced. Therefore, even when solubility parameters of both the solvent and polymer are equal, immersion of a crystalline polymer in the solvent at room temperature will have no effect. However as resin temperature is increased, appropriate solvents may become effective. As a result crystalline polymers such as polyethylene and polypropylene have no solvents at room temperature. Again this is only a generalization since few polymers are 100% crystalline and therefore some swelling may be realized due to the effect of the solvent in the amorphous regions of the polymer.

Solubility parameters for the liquids and some of the polymers of interest are shown in Figure 2-1. On this basis, some swelling of the polyethylene, ethyl cellulose and polytetrafluoroethylene (PTFE) in propane and PTFE in isobutane might be expected. Since polyethylene and PTFE are highly crystalline polymers they would not actually dissolve, however.

The solubility parameter for a given polymer can vary depending on the degree of hydrogen bonding of the solvent. Where available this range is given in Figure 2-1. The parameters for solvents and polymers were taken from references 3 and 4 except the parameter for isobutane which was calculated from thermodynamic properties.

Another method for predicting the chemical resistance of plastics to chemical environments has been proposed which is based upon the theory that a close match of the polarity of a solvent with the polarity of the primary polymer bond would indicate an incompatible service environment for a given polymer. By comparing the dielectric constants of the candidate polymers and the proposed OTEC working fluids, an estimation of the compatibility of the two systems may be made.

The values of dielectric constants for the plastics in Figure 2-1 range between 2.1 and 5.3 at a frequency of lkHz. Liquid ammonia and water have much higher constants while propane has a constant below the range for plastics. Solvation would not be predicted for any of the plastics based on dielectric constants.

Figure 2-1
Solubility Parameters of Solvents
and
Polymers
(@ 77 F)

	1.1	SOLVE	NTS	
	ISOBUTANE PROPANE		AMMONIA	WATER
<u>POLYMERS</u>	XX		×	×
AB\$				
ACETAL		X		
ACRYLIC	X			
CELLULOSE ACETATE		<b> </b>	4	
CELLULOSE ACETATE - BUTYRATE	<b>J</b> -		4	
ETHYL CELLULOSÉ	<u> </u>			
NYLON - 6		X		
NYLON - 6/6		×		
POLYCARBONATE	-	4		
POLYETHYLENE	<del>                                     </del>			
POLYETHYLENE TEREPHTHALATE	<del> </del>	X		an announcement of the state of
POLYPROPYLENE	<u> </u>			
POLYVINYLCHLORIDE	<u> </u>			
STYRENE ACRYLONITRILE				
POLYTETRAFLUROETHYLENE	X 10 2	0 30		0 50

SOLUBILITY PARAMETER (J/m³) 1/2 x10 3

#### Chemical Resistance Tables

The chemical resistance of a plastic is typically assessed in terms of changes in mechanical properties, appearance and dimensions after exposure of the unstressed plastic to a particular environment. Although changes in specific properties are sometimes reported, especially for "engineering" plastics, chemical resistance is generally expressed on a descriptive scale such as "poor-fair-good".

Chemical resistance data were compiled primarily from resin manufacturers, general references and pipe and tubing manufacturers. Emphasis was placed on the resistance of plastics to those fluids which most closely represent the proposed OTEC environments. The fluids selected were: ammonia, ammonium hydroxide, propane, heptane and sea water. Heptane was used as an indicator even though it is not a candidate working fluid since it is the lowest molecular weight alkane for which data are nearly always available. Information tended to be somewhat scarce on the low-boiling liquids as might be expected. References for the ratings are presented in Table 2-2. The resistance of PVC to propane, for instance, is listed as "good" in one source and "unacceptable" in another. Considering the many variations possible in a single family due to differences in additives, molecular weight, crystallinity, etc., this is understandable.

#### Long Term Load Bearing Capability

In the context of OTEC heat exchanger application, "strength" is the stress that a plastic can sustain for at least 100,000 hours. Some plastics possess physical properties such as creep resistance and tensile strength which may initially indicate that the material may be suitable for load bearing applications, but a closer investigation reveals that only considerably lower stress levels can be tolerated by these resins for long-term load bearing applications. Polycarbonate, for instance, excells in tensile strength, creep resistance and impact strength. However, under long-term loading, cracking or crazing may occur at strains of only 0.75%.

One approach to identifying plastics with adequate long-term load bearing capabilities is to select plastics commonly utilized in applications having something in common with the service conditions of an OTEC heat exchanger. The following thermoplastics are widely used for pressure piping, tubing, fittings and containers: acrylonitrile - butadene - styrene, acetal, cellulose, acetate butyrate, nylon, polybutylene, polyethylene, polypropylene and polyvinylchloride.

#### 2.3 CANDIDATE RESINS

In the selection of candidate resins to be subjected to testing and further evaluation as potential core materials for an OTEC heat exchanger, the previously described information on properties, chemical resistance and applications as reviewed. Of primary concern was the chemical resistance of the polymers to the proposed working fluids of the OTEC power plant. During the evaluation it soon became apparent that it would be unlikely that all resins selected would be chemically

Table 2-2
Chemical Resistance

	NH <sub>3</sub>	NH4OH	C <sub>3</sub> H <sub>8</sub>	I-C4H10	C <sub>7</sub> H <sub>16</sub>	H <sub>2</sub> O(salt)
Acetal	-	Ee		-	G <sub>e</sub>	E <sup>7</sup>
Acrvlonitrile-butadiene- Stvrene	-	F <sup>6</sup> -E <sup>15</sup>	-	-	F <sup>6</sup>	<b></b>
Cellulose Acetate	-	F <sup>7</sup>	S15	-	S <sup>15</sup>	E <sup>7</sup>
Cellulose Acetate- Butyrate	-	p15_p7	S <sup>15</sup>		X <sup>6</sup> -S <sup>15</sup>	E <sup>7</sup>
Nylon	F-G <sup>15</sup> +	G <sup>11</sup> -E <sup>7</sup>	G <sup>11</sup>	-	Ee	G11
Polybutylene	-	E 7	-	<b>-</b>	F <sup>7</sup>	E?
Polycarbonate		Xe -E15		-	€ <sub>e</sub>	-
Polyester	b11 .	P <sup>11</sup> S <sup>10</sup>	S10-G11	-	S10	S10-G11
Polyethylene (High Density)	P9 *S9+G11	S <sup>9</sup> -G <sup>11</sup>	P14-G11	-	p14_S9	S <sup>9</sup> -E <sup>7</sup>
Polyethylene (Med. & Low Density)	P9 -\$9+	S <sup>9</sup>	F14	-	p <sup>9</sup> _p <sup>7</sup>	S <sup>9</sup> -E <sup>7</sup>
Polypropylene	S <sup>9</sup> *+	E <sup>6</sup>	G12	-	Pe -Sa	S9 -E7
Polystyrene	S <sup>8</sup>	S8 -E6	S <sup>8</sup>	-	P7 -F7	S <sup>8</sup>
Polyvinylchloride	X13*-S8 +	G11-E6	X8 -G11	-	G13-E6	S8 -G11

- + Ammonia, Gas
- \* Ammonia,Liquid
- E Excellent
- G Good, No significant attack
- S Satisfactory
- F Fair, mild attack, limited use, polymer may be softened or swelled
- P Poor
- X Unacceptable

resistant to all three of the proposed working fluids. So that a fairly broad spectrum of commercially available plastics could be tested only the best suited member of each family (e.g. nylons, polyethylenes) was selected. Table 2-3 lists the seven plastics tested, the manufacturer and grade designation. Additional information on each plastic is contained in Appendix A.

Table 2-3
Core Material Candidates

<u>Plastic</u>	Resin Manufacturer	Grade	<u>Sample</u>
High Density Polyethylene (HDPE)	Soltex Polymer Corp.	F364	molded plaque
Polypropylene Homopolymer (PP)	Hercules, Inc.	PD-191 Type H	sheet
Polybutylene (PB)	Witco Chemical Corp.	Witron 4121	molded plaque
Polybinylchloride (PVC)	Firestone Plastics Co.	FPC 1437	molded plaque
Acetal Copolymer	Celanese Plastics Co.	Celcon-M-25-01	sheet
Nylon 11	Rilsan Corp.	BESNO	molded tensile bars
Cellulose Acetate (CAB)	Eastman Chemical	Uvex SN T44924	sheet

#### SECTION 3

#### CHEMICAL RESISTANCE TESTS

#### 3.1 GENERAL

Chemical resistance tests were the first experiments performed on the candidate plastics. The relative simplicity of these tests allowed a large number of environment/material combinations to be evaluated in a short time. Their purpose was mainly to screen the least suitable/materials from the development program rather than to produce information directly applicable to heat exchanger design. Non-stressed specimens of the plastics were conditioned in four liquids for a period of seven days. Chemical resistance was then assessed in terms of changes in tensile properties, weight and dimensions. Due to the short exposure duration, these data serve only as an indication of the behavior that a plastic might exhibit for a longer exposure.

#### 3.2 EXPERIMENTAL APPARATUS

Since the working fluids posed problems of pressure, flammability and toxicity, test equipment was designed to minimize these and maintain the test specimens at the desired temperature. Specimens were exposed to working fluids in small pressurized containers consisting of a section of 2 inch schedule 40 aluminum pipe, 8 inches long with end caps secured by victaulic couplings which allowed the containers to be opened and closed frequently and easily. This container is shown in Figure 3-1. A separate container was provided for each type of plastic being tested. Six containers were immersed in a water-filled, closed tank which was maintained at 80 F by an external, constant temperature circulating bath. The water level in the tank was held constant by a float valve that admitted makeup water. A blower provided induced ventilation of the air space above the water. Besides serving as a constant temperature medium, the water revealed any leaks in the containers and dissolved any minor leakage of ammonia gas.

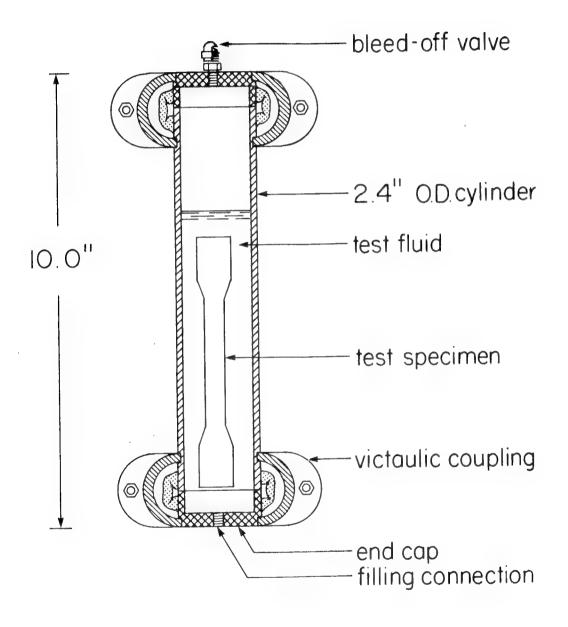
A manifold was provided for evacuating, filling, venting and purging the containers. Over pressure protection for the containers was provided by relief valves in the manifold set at 250 psig against the possibility of a temperature control malfunction. Manifold components were stainless steel except for air, vacuum and low pressure vent lines which were nylon tubing. Figure 3-2 is a schematic of the working fluid exposure apparatus.

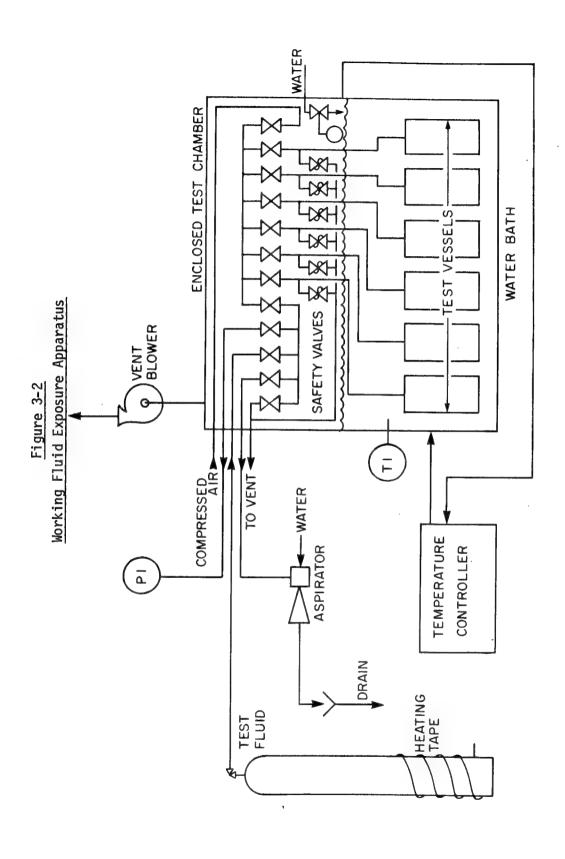
Sea water for the tests was obtained from the Florida Atlantic University Marine Materials and Corrosion Laboratory and was natural except that most organisms were removed by sand filtration. The anhydrous ammonia was of 99.99% purity, while the isobutane and propane were 99.0% pure.

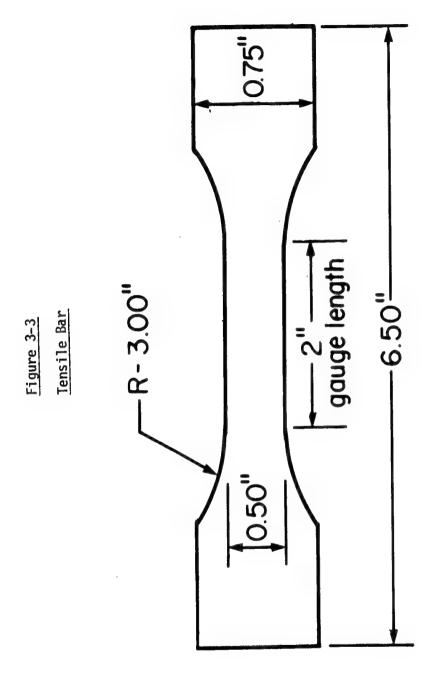
#### 3.3 PROCEDURES

ASTM Type I tensile bars having a gage width of one half inch and gage length of two inches were die cut from sheets or plaques for six of the candidate plastics. The dimensions of these tensile bars are shown in Figure 3-3.

Figure 3-1
Specimen Container







To account for orientation effects, particularly with extruded sheet, specimens were cut both parallel and perpendicular to an axis of the sheet or plaque. Orientation, identification number and type of plastic were marked in the grip area of each specimen. Die cutting tended to produce defects in the specimen edges so it was found necessary to remove these by mechining to obtain reproducible tensile test results. Nylon-II specimens were obtained as injection molded Type I tensile bars and required no further preparation.

Tensile bars for the hydrocarbon tests were cut in the "X" or perpendicular direction only. It was found in earlier tests in sea water and ammonia that orientation was not a significant factor in the tensile test results.

All specimens were conditioned at 80 F and 50% relative humidity for a minimum of 88 hours using ASTM standard method D618 as a guideline. This was done to bring the specimens to a common starting point since moisture absorption can significantly effect properties of several of the candidate plastics. Conditioning was done in closed plastic containers in which relative humidity was maintained at approximately 50% by a saturated aqueous solution of calcium nitrate (not in contact with the specimens).

Tensile properties testing was done using ASTM Standard method  $D638^{16}$  as a guide. For the control tests, three specimens each of "X" and "Y" orientation were tested. The thickness and width of each specimen was measured at three locations in the gage length to determine an average and minimum cross sectional area. Specimens were mounted in an INSTRON TM-S testing machine and pulled at a crosshead speed of 0.20 inches per minute. Tensile load versus grip separation curves were automatically recorded.

Before exposure to sea water or working fluids, specimens were weighed and gage dimensions measured. For sea water exposure six specimens of each plastic (three of each orientation) were tested. Four specimens of each plastic (two of each orientation) were exposed to ammonia and two specimens of each were exposed to propane and isobutane.

For working fluid exposure each type of plastic was placed in a container which was alternately evacuated and pressurized with vapor several times to remove air. A pressure differential between the working fluid supply bottle and the containers was created for filling the containers by warming the bottle to  $90\text{-}95\ F.$ 

Filling progress was monitored by weighing each container. Attempts were made to measure internal liquid level of ammonia by measuring electrical resistance between an insulated probe and the body of the container. This method proved unsatisfactory although the technique has been used successfully by others. After seven days exposure to working fluid the containers were slowly vented to atmosphere followed by alternate evacuating and purging with compressed air. Upon removal from the containers the plastic specimens were immediately weighed and measured for comparison with the original values. Sea water tests were similar except that it was not necessary to use pressurized containers. Specimens were immersed in sea water in closed containers and held at 80 F. In addition to seven day tests, exposures of about 130 days were also done in sea water.

#### 3.4 RESULTS AND DISCUSSION

Tables 3-1, summarizes the changes in weight, dimensions and mechanical properties of the seven candidate plastics. These data are presented graphically in Figures 3-4 through 3-10. These curves were obtained by averaging the individual specimen curves and they serve to illustrate the general performance of each plastic.

Conventional yield stresses, the stress at which the tangent to the stress-elongation curve has zero slope, were exhibited by the majority of plastic-environment combinations. Where well defined yield stresses were not encountered, the reported value is the stress at 5% offset. Grip separation and not gauge length extension was monitored during the tensile tests and these data were used for all calculations. Consequently, the elongation and modulus data should be viewed as qualitative.

The mode of failure, either fracture or drawing with no fracture, tended to be characteristic of the material and not dependent upon environment. Although there were few exceptions, the environments used appeared to have no significant effect on the type of failure, except for changes in percent elongation at failure.

Tensile properties obtained in the control tests for several of the plastics are lower than those reported by the manufacturers primarily because of the difference in testing speed. It is customary, for instance, to test the polyolefins at crosshead speeds of 2 and 20 inches per minute rather than 0.2 inches per minute as used here. Tests 79 through 85, listed in Appendix B were conducted at 2.0 inch per minute and produced the following increases in maximum tensile strength over tests at the slower speed.

Test #	<u>Plastic</u>	% Increase
79	HDPE	29
80	Polypropylene	25
81	Acetal	14
82	PVC	24
83	Nylon-11	16
84	CAB	2 .
85	Polybutylene	. 8

The polyolefins and PVC exhibited excellent resistance to weight and dimensional changes for sea water exposures. Acetal, nylon and CAB however, indicated slight hydrophilic tendencies. With the exception of nylon and CAB, the plastics exchibited an increase of tensile properties subsequent to sea water exposure which appeared to be at the expense of ductility (reduced strain to fracture). A comparison of the seven day sea water test results with those of the longer exposures (127-131 days) reveals that in most cases a major percentage of the total property change after the longer exposure occurred in the first week.

Only acetal was highly resistant to all three potential working fluids although considerable swelling and modulus reduction occurred in ammonia. The polyolefins also exhibited good-to-excellent resistance to ammonia with only slight

Chemical Resistance, 7-day Exposure at 80 F

TENSILE PROPERTIES	* NOTH	OT A	94 10			0.303 61	0.179 36	1.51 100 Drawing, No Rupture		1,24 82		0.957 64 Drawing, No Rupture	1.70 100 Drawing, No Rupture		1.96 115 "	6 H	
TENSIL	1 &		100	107	92	51	70	100	107	102	87	886	100	TI	101	77	
	POTE		191	2121	1828	1010	1376	2840	3041	2883	2475	2772	4102	4546	4147	3165	
	1 4 E	3	IÄ	105	95	09	F	100	107	102	87	80	100		101	77	•
	ROWALD NOISE	The Account	2372	2498	2258	1434	1682	2840	3041	2883	2475	2772	4102	4546	4147	3165	
	FORME HE	WHITE	0	0	0.3	3.6	4.0	0	0	0.3	<b>∞</b>	0.7	.0	0	0.3	1,4	
		Eq.	0	0	. 8° 0	7.8	დ ლ	0	0	0.4	ຕຸ	1.6	0	0	0.7	60	
	Managa	EO TOST	AIR	SEA WATER	LIQUID AMMONIA	LIQUID PROPANE	LIQUID ISOBUTANE	AIR	SEA WATER	LIQUID AMMONIA	LIQUID PROPANE	LIQUID ISOBUTANE	AIR	SEA WATER	LIQUID AMMONIA	LIQUID PROPANE	
<del></del>				····	LAPE	ruax	10d	21	EME	HXFI	XEL	LOI	ENE	)bar	ХРК	ьог	•

21

Table 3-1
Chemical Resistance, 7-Day Exposure at 80 F
(Con't)

			\$3 <sub>NV</sub>	242	Ą	\	13	•		
	MEDIUM .	Tita	SNOWING TO THOUGH	ALO MOTS REDITA	to to	NOTINGIA NOTINGIA	A HICAGORIS	TST OT X STAROOK WOTHERS		SINGLAND
AIR		0	0	4267		3380	100	1.749	100	
SEA	SEA WATER	0.	0.1	3623	85	2892	98	1.618	93	
LIQ	LIQUID AMMONIA									Specimens dissolved
rig	LIQUID PROPANE	2.8	e e	2635	62	2111	62	1.22	. 70	Slight Yellowing
LIC	LIQUID ISOBUTANE	H .2	0.8	3800	68	3018	89	1.386	79	. ·
AIR		0	0	6360	100	6330	100	3,301	100	-
ZE/	SEA WATER	0	<b>o</b>	6832	107	6832	108	3,761	114	
Ĕ	LIQUID AMMONIA	10.7	4.0	978	15	921	. 51	1.167	35	Discolored, Rubbery
LI	LIQUID PROPANE	0.0	0.0	7719	106	6744	107	4,35	132	Drawing, No Rupture
LI	LIQUID ISOBUTANE	0.0	0.0	7065	111	7065	112	3:431	104	<b>=</b>
									•	

22

Chemical Resistance, 7-Day Exposure at 80 F (Con't)

9 0 0 9 0	STIMETION OF TRIVIAL	THOUGHT AS STREET TO THE TOTAL	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0 - 4171 100 1.06 100 Drawing, No Rupture	0 4121 99 0.952 90 "	0.8 2865 - 2694 65 0.409 39 "	-5.6 4673 - 4284 103 0.950 90 "	0.1 4305 103 1.04 99 "		0 8226 100 8226 100 3.45 100	0 8572 104 8572 104 3.60 104	2.1 8045 98 8045 98 1.69 49	0.1 8413 102 8413 102 3.51 102	0.4 8585 104 8585 104 3.16 92
AIR SEA WATER LIQUID AMMONIA LIQUID ISOBUTANE LIQUID AMMONIA IQUID AMMONIA IQUID PROPANE		* ADMINIS CHO!	NO STATE OF THE PARTY OF THE PA			.0	٠ <u>.</u>			0	0.2 0			
		MEDIUM		ALK	SEA WATER	LIQUID AMMONIA	LIQUID PROPANE	LIQUID ISOBUTANE		AIR	SEA WATER	LIQUID AMMONIA	LIQUID PROPANE	LIQUID ISOBUTANE

Figure 3-4
Tensile Curves of Polybutylene

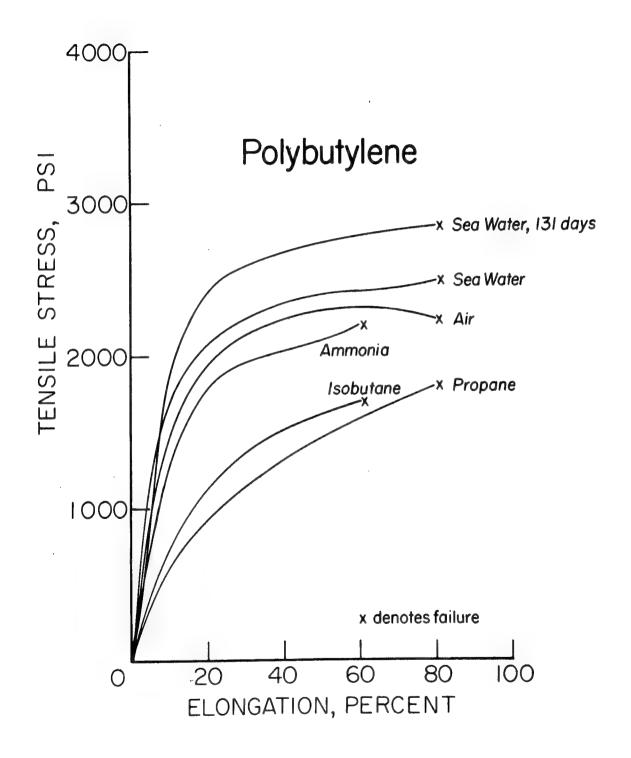


Figure 3-5
Tensile Curves of High Density
Polyethylene

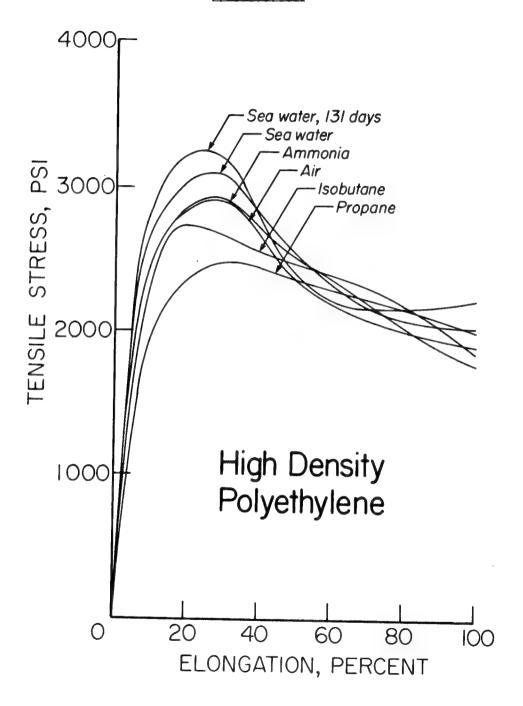


Figure 3-6
Tensile Curves of Polypropylene

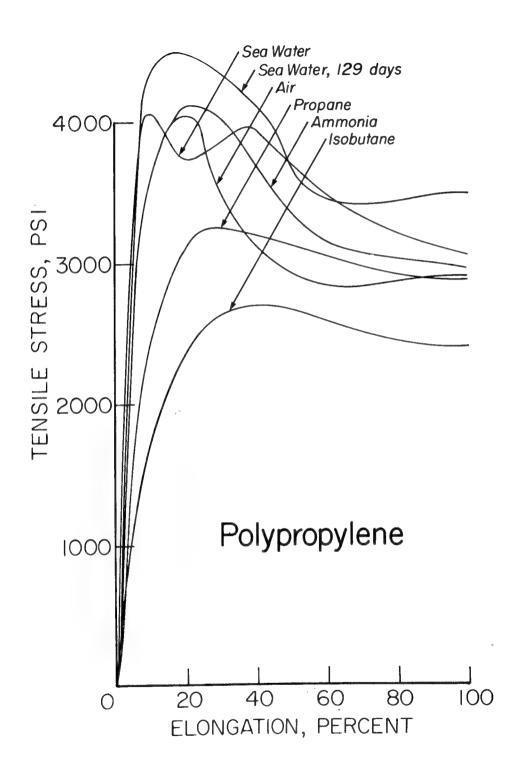


Figure 3-7
Tensile Curves of Nylon 11

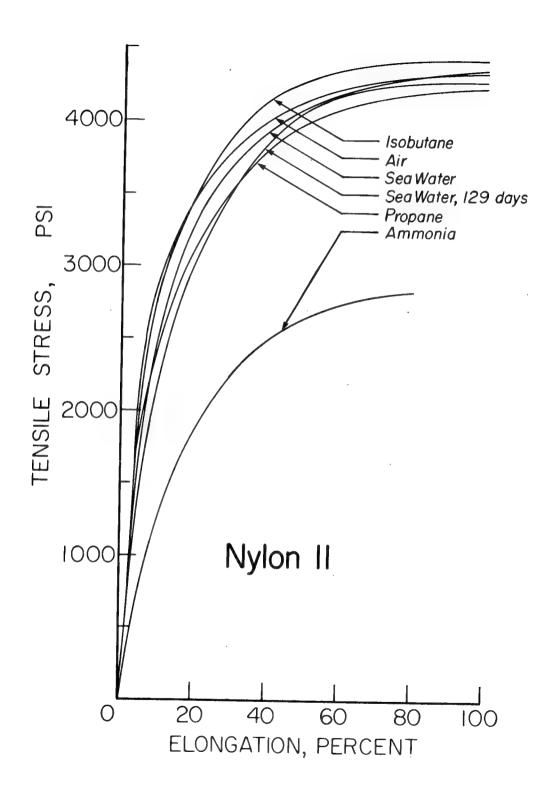


Figure 3-8
Tensile Curves of Acetal

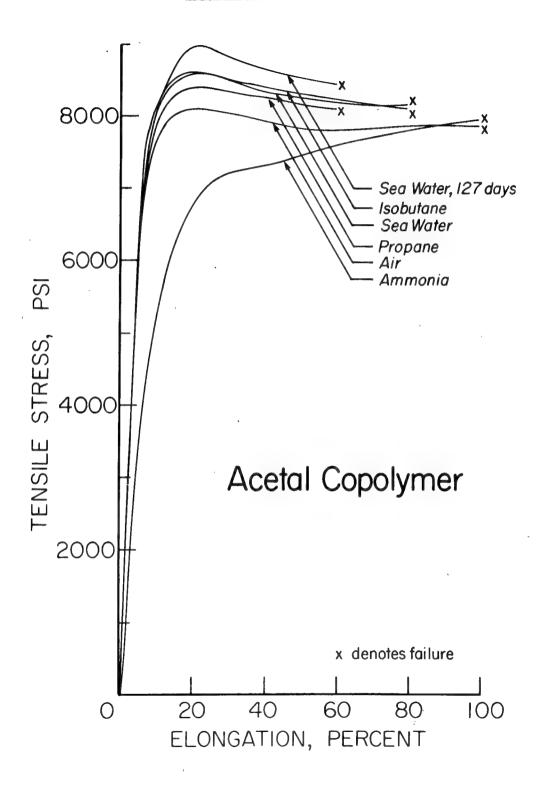


Figure 3-9
Tensile Curves of Cellulose
Acetate Butyrate

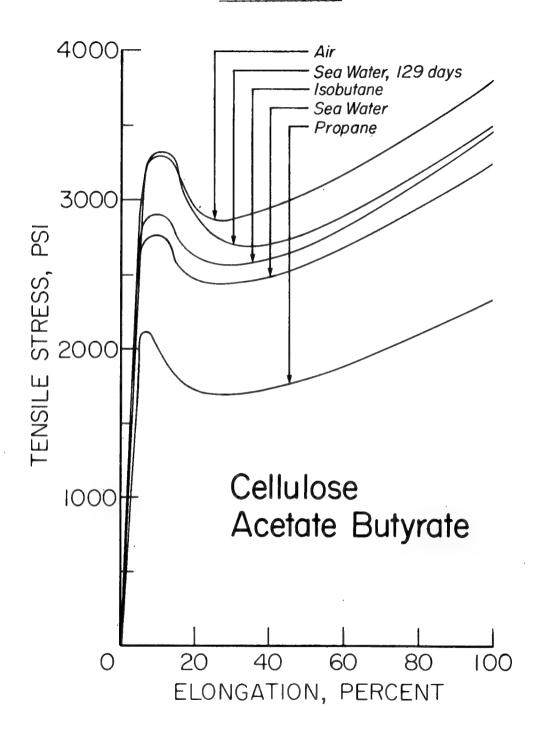
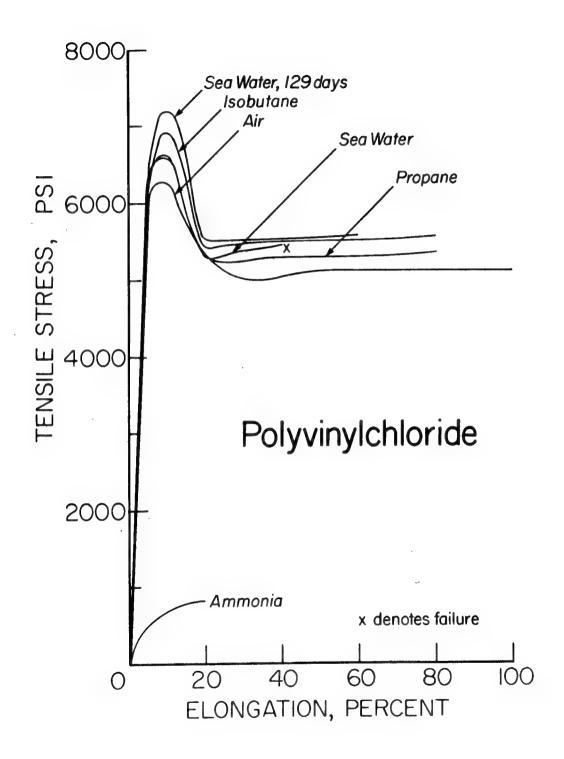


Figure 3-10
Tensile Curves of Polyvinylchloride



swelling evident. The tensile properties of PVC and, to a lesser extent, nylon were reduced by exposure to ammonia, with severe swelling of PVC also occurring. CAB exhibited severe reaction to this environment which prevented evaluation of the specimens.

The effects of propane were generally more pronounced than those of isobutane. The resistance of nylon, PVC and acetal to both hydrocarbons was excellent. In addition, CAB and polyethylene exhibited good resistance to isobutane.

Comments on each plastic follow:

High Density Polyethylene. As with the other two polyolefins, HDPE faired the best in sea water and ammonia but showed some swelling in isobutane and propane and loss of strength in the latter. Of the 26 HDPE specimens tested in all environments, 22 formed stable necks and drew without rupture. Failure by necking rupture occurred in two specimens exposed to ammonia and one exposed to propane.

<u>Polypropylene Homopolymer</u>. The chemical resistance of polypropylene was comparable to HDPE except for isobutane exposure. Cold drawing occurred in all cases except the two specimens exposed to propane which ruptured at about 75% elongation.

<u>Polybutylene</u>. Unlike the other two polyolefins, polybutylene showed a slight loss of properties after exposure to ammonia. The effects of hydrocarbon exposure were also more pronounced. It is possible that the polybutylene specimens contained small internal voids since some were encountered during specimen preparation. Data scatter for these tests was not particularly high however.

<u>Polyvinylchloride</u>. Resistance of PVC to the hydrocarbons and sea water was excellent. Ammonia appeared to plasticize PVC to a considerable extent; the tensile bars became rubbery, almost returning to their original length after tensile testing. Furthermore, after standing for a few days in air after testing, the ammonia evaporated and the tensile bars again became rigid. Some of the discoloration also disappeared upon standing.

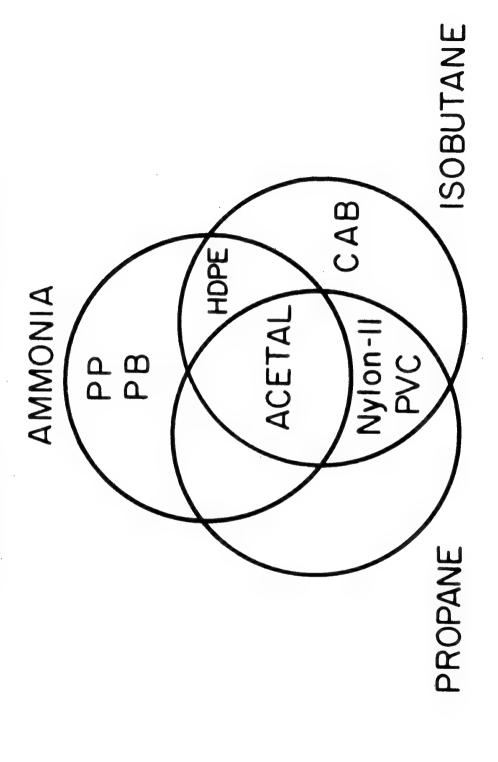
Acetal Copolymer. Acetal demonstrated the best all-around resistance of the seven plastics tested. A reduction in modulus and swelling resulted from exposure to ammonia were the only pronounced effects observed.

Nylon-11. Resistance to sea water and the hydrocarbons was excellent but ammonia resistance was only fair.

<u>Cellulose Acetate Butyrate</u>. CAB showed some loss of properties in all of the fluids although resistance to sea water and isobutane was good. A severe reaction with ammonia occurred which was presumably ammonolysis of the cellulose esters of which CAB is composed.

Compatability of the candidate materials with possible OTEC working fluids is indicated generally by the diagram in Figure 3-11.

Figure 3-11 Compatibility of Candidate Materials with Working Fluids



All materials demonstrated good or excellent short term resistance to sea water at 80 F but only acetal was highly resistant to all four fluids. It was expected that propane and isobutane would affect the physical properties of a given plastic to an equivalent extent but this has not proved to be the case.

Acetal, nylon-11 and PVC would be chosen for further development work leading to heat exchangers for a propane or isobutane system. In the interests of compatibility with the overall DOE Ocean Thermal Energy Conversion Program, however, all subsequent development work was oriented toward ammonia working fluid. High density polyethylene, polybutylene and acetal were therefore chosen for further consideration.

## SECTION 4

## ENVIRONMENTAL RUPTURE TESTS

## 4.1 GENERAL

As previously noted, the chemical resistance tests were intended to screen candidate materials rather than produce useful design data. The environmental rupture tests, on the other hand, provided the following: 1) information on the dependence of tensile failure stress on time and environment; 2) a gross indication of susceptibility to environmental stress cracking; and 3) creep extension and modulus information under constant load. To obtain this type of information, plastic specimens must be subjected contemporaneously to stress and environment.

It was necessary to develop a test apparatus to meet the following requirements: 1) maintain test specimens in a high pressure environment; 2) apply a known constant load to the specimens; 3) allow measurement of specimen deformation; and 4) allow determination of specimen failure time. The number of environment/material combinations for these tests was necessarily smaller than for the preceding tests. The environments were confined to sea water, liquid ammonia and air (for controls). Materials were limited to those resistant to ammonia; HDPE, acetal and polybutylene. Three compounds of HDPE were tested; unfilled, 10% loading and 15% loading.

## 4.2 EXPERIMENTAL APPARATUS

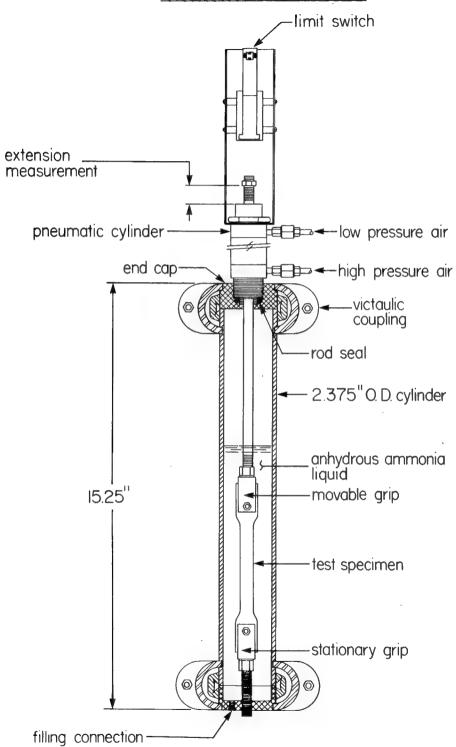
ASTM Method D2990 $^{16}$  was used as a guideline to develop testing procedures. Specimen configuration was ASTM Type I tensile bar with some minor modifications. The ends of the specimens were designed to accept special grips. The specimen cross sectional area in the gage length was reduced in order to meet operating limits of the test apparatus.

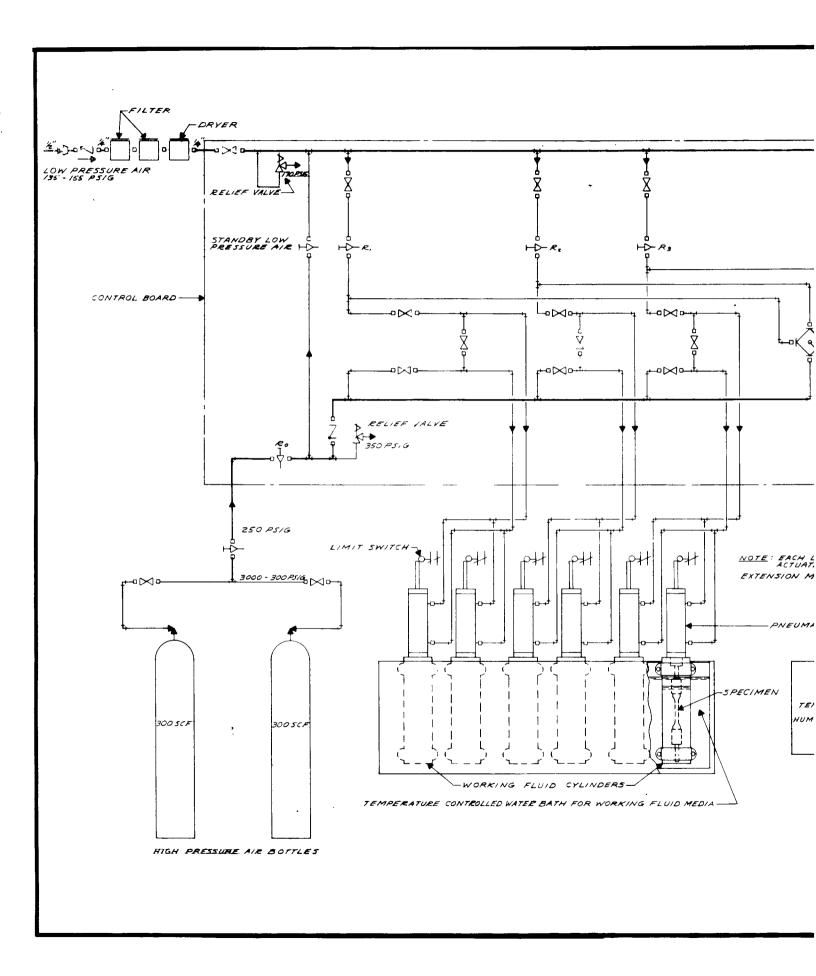
Loads were applied to the test specimen by pneumatic cylinders. The primary reason for using these cylinders was to enable testing in liquid ammonia at 80 F. Figure 4-1 illustrates an ammonia test station of which six were constructed. A double acting, double rod pneumatic cylinder was mounted on a vessel similar to those used for the chemical resistance tests. The internal rod end was attached to the tensile specimen and the outside end was used as an extension indicator. A limit switch actuated by the rod operated a timer to record time of failure. To prevent ammonia from contaminating the compressed air in the pneumatic cylinder, the high pressure side was maintained at an air pressure about 10% greater than that of the ammonia in the test vessel. In addition, a rod seal was employed to further reduce the possibility of leakage.

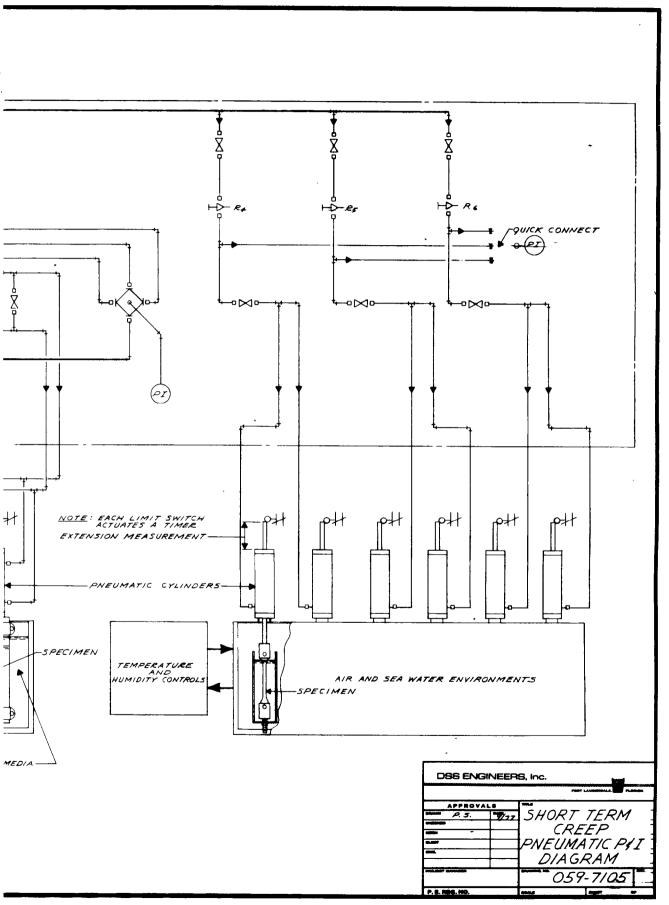
Compressed air to operate all cylinders was provided by a system of valves and regulators from an air compressor and high pressure air bottles. To determine the pressure-load relation for the pneumatic cylinders, a pressure versus extension curve was obtained for a spring whose force-extension characteristic was determined on an Instron. Drawing No. 059-7105 is the P&I diagram for the pneumatic system.

Figure 4-1

Ammonia Test Station for
Environmental Rupture Tests







For air and sea water tests, a six station apparatus was constructed. The specimens were enclosed in a plexiglas box in which the air was controlled at 80 F and 50% relative humidity. During the sea water testing, each individual specimen was immersed in an acrylic seawater bath.

# 4.3 PROCEDURES

The scatter of creep-rupture data is considerable with one half to a full decade of variation in time-to-failure being typical. Therefore, it is necessary to test two specimens at each stress level to obtain satisfact-ory results. The gage dimensions of testing specimens were first measured. The measurements of cross sectional area of two specimens being tested at the same stress level must agree with each other within 2% in order to minimize error in computing applied stress.

Specimens for the control tests in air were preconditioned for 96 hours at 80 F and 50% RH before application of tensile loads. For sea water and ammonia tests, specimens were preconditioned in their respective environments for 24 hours in an unstressed condition. Tests in ammonia were initiated in the following sequence. The specimen was clamped in the grips, the cylinder assembled and the ammonia filling connection made. An equal air pressure of approximately 160 psi was applied to both sides of the pneumatic cylinder by opening the crossover valve on the control board. Next, ammonia was admitted to the test cylinder by the same general procedure used for the chemical resistance tests. At this point there was a small load on the specimen caused by the vapor pressure of the ammonia liquid acting on the pneumatic cylinder rod area. After preconditioning, the desired load was applied by first setting the low pressure regulator, closing the crossover valve and then bleeding off excessive air pressure on the low pressure side of the cylinder by slowly opening the low pressure air valve.

Because only rod extension (grip separation) could be measured for ammonia tests, grip separation was correlated with gage length extension by measuring both simulaneously for the control test of longest duration for each type of plastic. Rod extension measurements were made only during the tests at the three lowest stress levels having nominal durations of 30, 100 and 300 hours.

# 4.4 RESULTS AND DISCUSSION

## <u>Unfilled Plastics</u>

Tensile stress versus time-to-failure curves for HDPE, acetal and polybutylene are presented in Figures 4-2, 4-3 and 4-4, respectively. Specimen failure was defined as rupture or drawing to the full stroke of the apparatus. The failure mode of HDPE in all environments was by drawing. Acetal and polybutylene failed by rupture except that drawing of acetal occurred in ammonia. The curves which are typically straight lines with negative slopes on log-log plots, are least-squares fits of the data points. Failure stress for HDPE and acetal were time dependent whereas polybutylene exhibited nearly horizontal lines. The largest scatter was exhibited by polybutylene. This is probably attributable to small

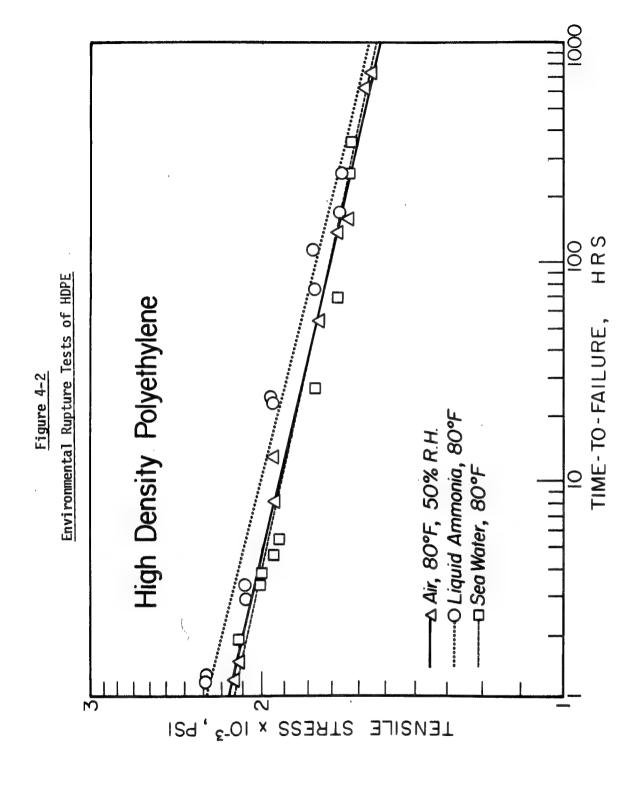


Figure 4-3
Environmental Rupture Tests of Acetal

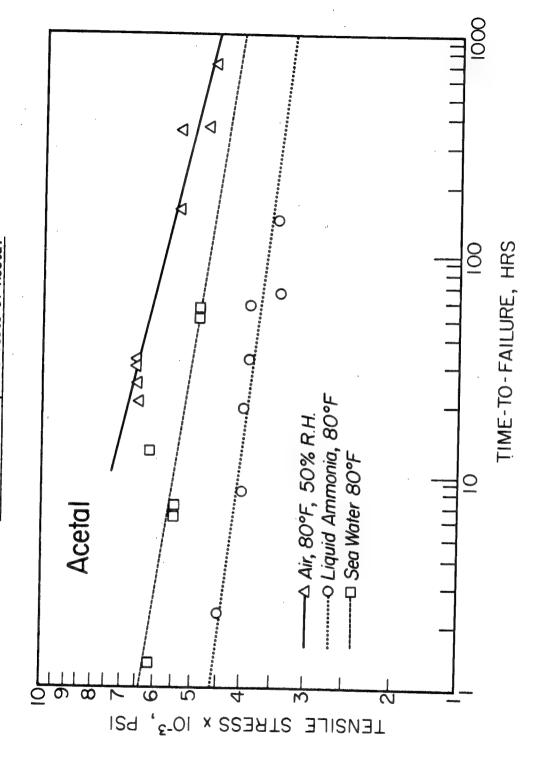
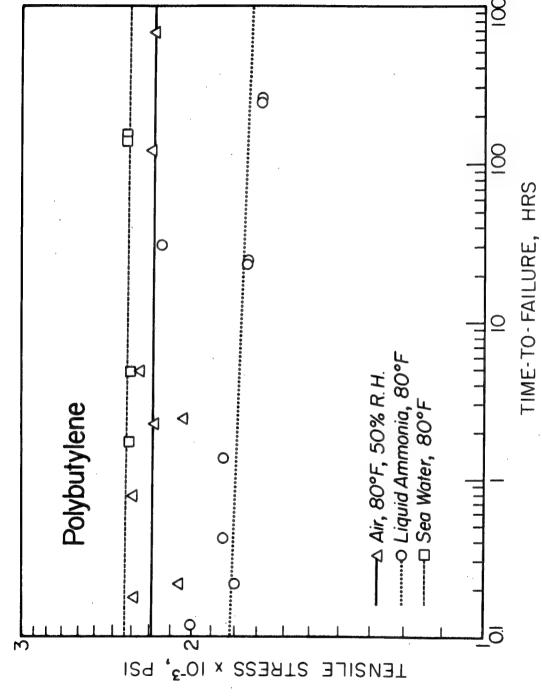


Figure 4-4
Environmental Rupture Tests of Polybutylene



small voids in the plastic as these were often encountered during specimen preparation. Agreement between the control tests in air and published data for each type plastic was good.

With the measurements of initial gage length and gage extension at any given time, the creep strain may be obtained by definition, i.e.,

Creep strain = gage length extension : initial gage length. (4-1)

The creep strain vs. time curves for HDPE, Acetal and Polybutylene in various environments are shown in Figures 4-5, 4-6 and 4-7 respectively.

The load-bearing ability of HDPE was essentially unaffected by sea water or ammonia. Acetal is perhaps the most interesting case because the pronounced reduction in failure stresses in ammonia and sea water would not have been expected from the chemical resistance data in Section 3. The extrapolated curves converge, however, so that the reduction in load-bearing ability at longer time of practical interest, such as 100,000 hours, would be slight.

A transition from ductile to brittle failure, caused by stress cracking, would be evidenced by drooping rather than linear stress versus time-to-failure curves if it occurred within the duration of the tests. On this basis, none of the three plastics appeared to be highly prone to environmental stress cracking in ammonia or sea water. This is a rough generalization since applied stresses in these tests were essentially uniaxial. A need for more specialized environmental stress cracking tests such as the bent strip, eliptical jig or cracked plate tests is not indicated by these results.

These experiments were designed primarily to produce stress vs. time-to-failure information and stresses were therefore selected to obtain the desired spread in failure times. The range of stresses is consequently too narrow to allow good correlation of the creep strain data via stress-time superposition. So that some comparison can be made of the effects of environment and filler addition on creep strain, data have been organized by a creep modulus equation. The creep (apparent) modulus is defined as:

Creep Modulus = Initial Applied Stress - Creep Strain (4-2)

Kinney<sup>17</sup> has developed a three-coefficient creep modulus equation to describe the creep data, i.e.

 $E = (A+B \log t) / (1+C \log t)$  (4-3)

Where E is the creep modulus at time t, and coefficients A, B and C are empirically selected so that the equation fits observed data as best it can. Coefficient A represents a creep modulus at unit time such as one (1) hour. It has the same unit as modulus, i.e., psi. Values for coefficient A are comparable with, but usually less than, the observed modulus values. Coefficient B is identified as a slope index. It corresponds to the slop of a plot on semilogrithmic coordinates for the special case that the denominator of Eq. (4-3) has a value of unity. This slope

Figure 4-5 Creep Strain Curves of HDPE

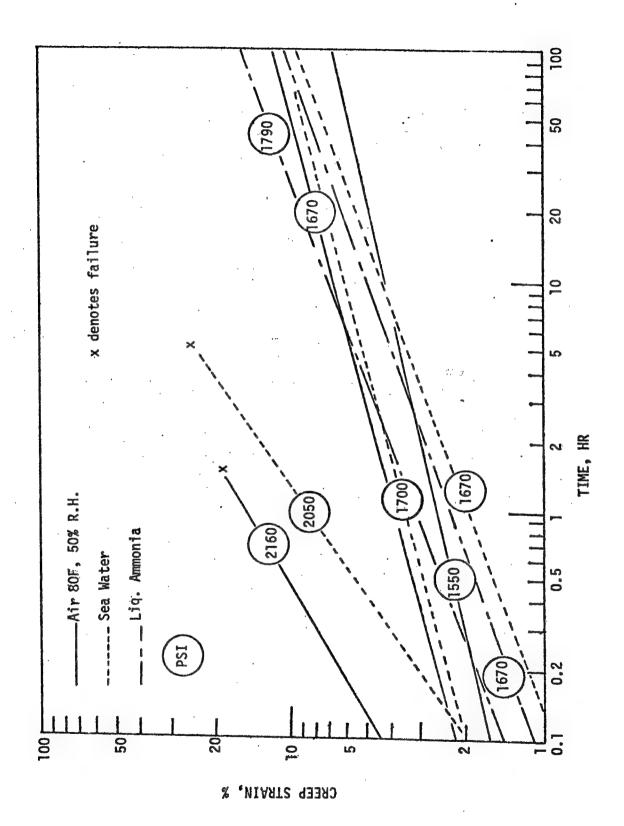


Figure 4-6 Creep Strain Curves of Acetal

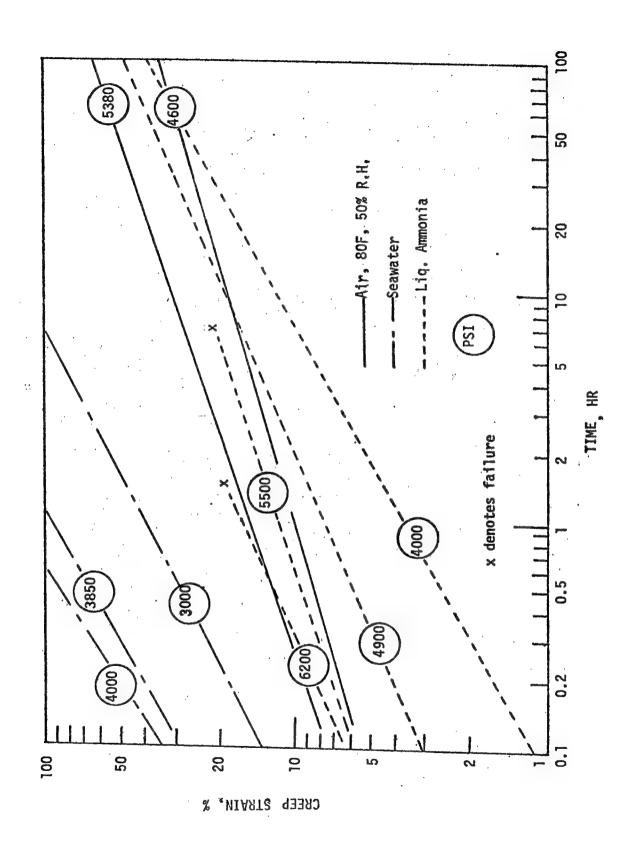
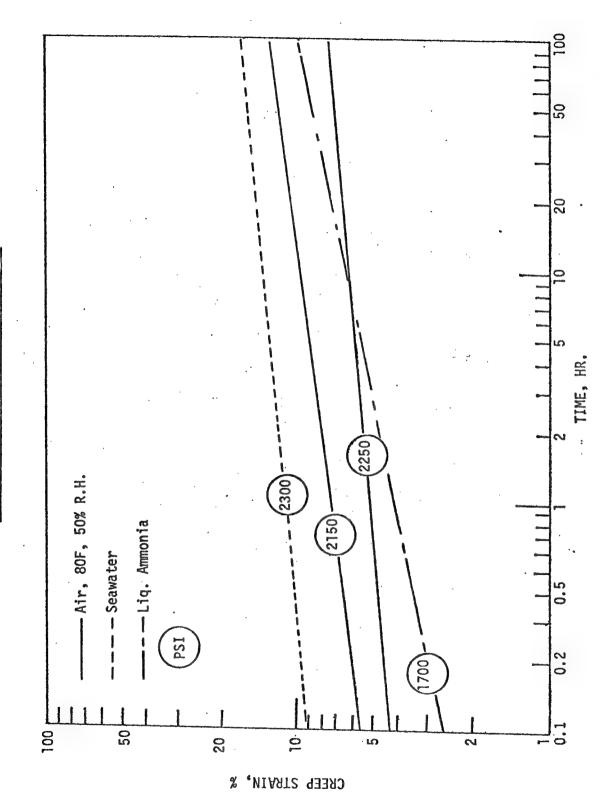


Figure 4-7 Creep Strain Curves of Polybutylene



index has the same unit as coefficient A. Usually, it is a negative value with a magnitude only a fraction of that for coefficient A. Such a negative sign may be interpreted as the tendency of the creep modulus to decrease with time. The third coefficient of Eq. (4-3), coefficient C, is the curvature index which represents departure of the relation between modulus and time from a semi-logrithmic plot. It is dimensionless and ordinarily shows a small positive fractional value.

After the creep modulus was calculated from creep strain and initial applied stress, the coefficients A, B, and C in Eq. (4-3) were determined by curve fitting. In Table 4-1, coefficients A, B. and C of Kinney's equation are listed for HDPE, acetal and polybutylene in air, sea water and ammonia liquid.

Based on the coefficients shown in Table 4-1 and Kinney's equation, isochronus stree-modulus curves for HDPE, acetal and polybutylene have been plotted in Figures 4-8, 4-9 and 4-10, respectively. Due to the scattering of polybutylene experimental data, only three lines are presented in Figure 4-10. These figures are for a maximum time of 100 hours and are only for comparison of plastic behavior in various environments. All the curves display the normal negative dependence of modulus on applied stress. In general, ammonia and sea water environments caused an increase in modulus of HDPE at corresponding stresses and test times. The modulus of acetal was considerably reduced in ammonia while sea water had little influence in spite of the fact that acetal is slightly hydrophilic. While there is no direct relationship between creep modulus and time-tofailure there is a tendency for a change in one to be accompanied by a qualitatively similar change in the other so long as this material remains ductile. This is illustrated by the case of acetal in ammonia; both time-to-failure and creep modulus for equivalent stress decreased in that environment.

If the lowest stress vs. time-to-failure curve for each plastic is extrapolated to 100,000 hours, failure stress for HDPE, polybutylene and acetal are respectively, 1057, 1585 and 2115 psi. Using these stresses in the evaluation formula presented in Section 2 shows that HDPE has a slight advantage over acetal and that acetal is far superior to polybutylene. This indication and proven suitability for surface make HDPE the material of choice for subsequent development work.

## Filled HDPE

The same type HDPE resin used for the previous mechanical tests was compounded with 10% and 15% by weight acetylene black in order to improve its thermal conductivity. The discussion and measurements of thermal conductivity of unfilled and filled HDPE are presented in Section 5.

Since the mechanical properties and the chemical resistance of these filled compounds may differ from unfilled HDPE, it is necessary to perform the tensile tests and environmental rupture tests to identify any difference between the unfilled and the filled HDPE.

The tensile tests were very similar to the chemical resistance tests except the tests were performed in a controlled air environment. The results are shown in Figure 4-11 and listed in Appendix as Test No. 191

TABLE 4-1

# COEFFICIENTS OF KINNEY'S EQUATION FOR UNFILLED PLASTICS

# CONSTANTS IN

			KINNEY CREEP MODULUS EQUATION	
SYSTEM	STRESS	Υİ	<u>B</u>	ပျ
HOPE-AIR	1554	×	-9.5183 x 10 <sup>3</sup>	2 × 10
	1671	4.7767 × 10 <sup>4</sup>	-1.5203 x 10 <sup>4</sup>	2.6552 x 10 <sup>-1</sup>
	2102	×	-3.2505 x 10 <sup>4</sup>	3.8593 x 10 -2
HDPE-SEA WATER	1665	8.6055 x 10 <sup>4</sup>	×	$5.6063 \times 10^{-1}$
	1697	. x 6538	×	1.8540 x 10 -1
	1738	4.6233 x 10 <sup>4</sup>	-1,3366 x 10 <sup>4</sup>	2.7182 x 10 <sup>-1</sup>
	2050	2.8634 × 10 <sup>4</sup>	×	1.0498 x 10 <sup>-1</sup>
HDPE-AMMONIA	1673	8.6088 × 10 <sup>4</sup>		$1.4780 \times 10^{-1}$
	1792	×	× 680	3.1762 x 10 <sup>-1</sup>
	1955	×	-6.1722 x 10 <sup>4</sup>	4.4609 x 10 <sup>-1</sup>
ACETAL-AIR	4601	×	194 ×	1.7317 x 10 <sup>-1</sup>
	5379	×	$-1.6219 \times 10^{5}$	-3.0815 x 10 <sup>-2</sup>
ACETAL-SEA WATER	4900	$6.2087 \times 10^{5}$	0524 x	5.3012 x 10 <sup>-1</sup>
	5500	×	×	$-1.1962 \times 10^{-2}$
	6200	×	2242 x	-8.213 x 10 <sup>-2</sup>
ACETAL-AMMONIA	3400	0191 x	×	1.6392 x 10 <sup>-2</sup>
	3850	×	1799 x	-2.2622 x 10 <sup>-1</sup>
	4000	×	0055 x	4.4676 × 10 <sup>-1</sup>
POLYBUTYLENE-AIR	2150	×	×	$-7.0603 \times 10^{-2}$
	2250	×	×	2.6566 x 10 <sup>-1</sup>
	2275	1.3456 x 10 <sup>4</sup>	×	-1.7005 x 10 <sup>-1</sup>
POLYBUTYLENE-SEA WATER	2300	×	$-8.9716 \times 10^{3}$	-2.6379 x 10 -1
POLYBUTYLENE-AMMONIA	1700	5.2351 x 10 <sup>4</sup>	×	-1.2551 x 10 -1
	1850	$-7.2311 \times 10^{4}$	-6.8565 x 10 <sup>5</sup>	-9.1118 x 10 <sup>-1</sup>

Figure 4-8 Isochronous Stress-Modulus Curves of HDPE

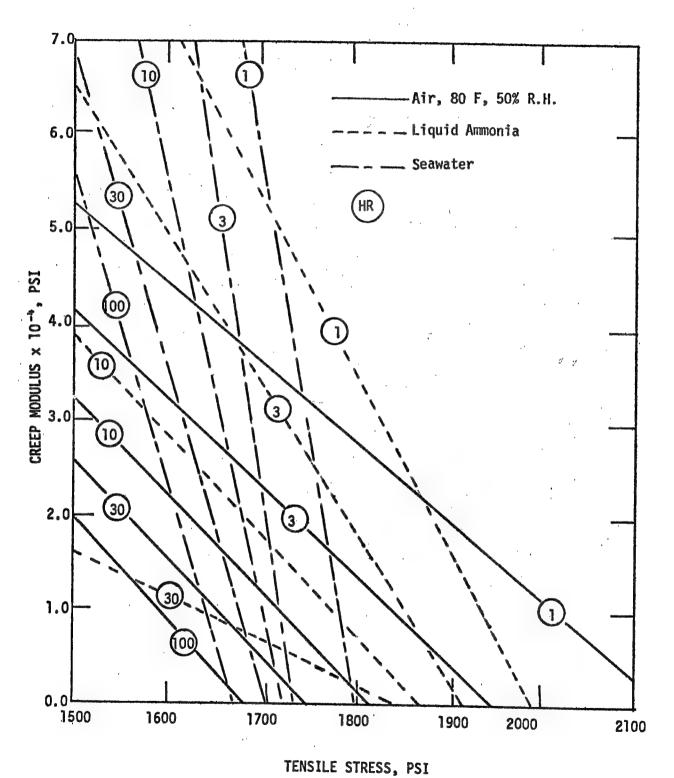


Figure 4-9
Isochronous Stress-Modulus Curves of Acetal

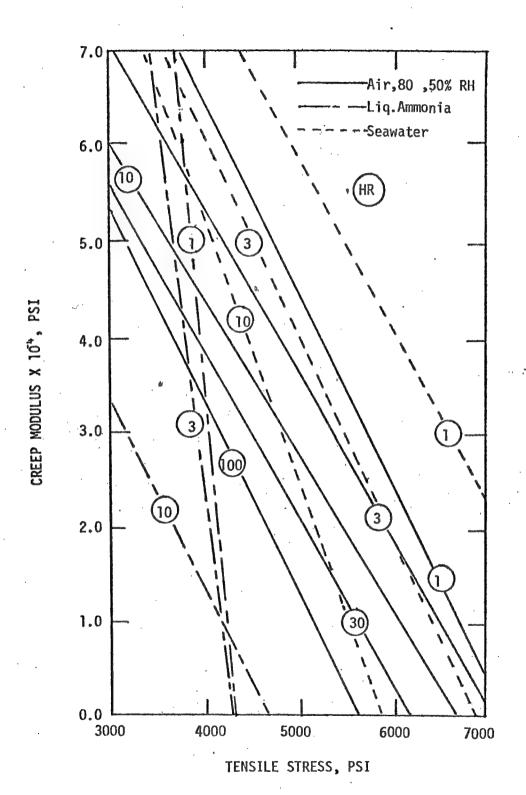
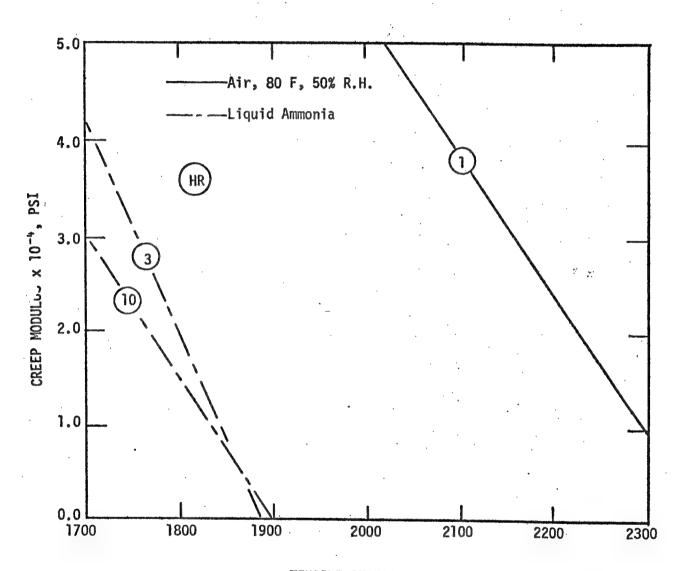
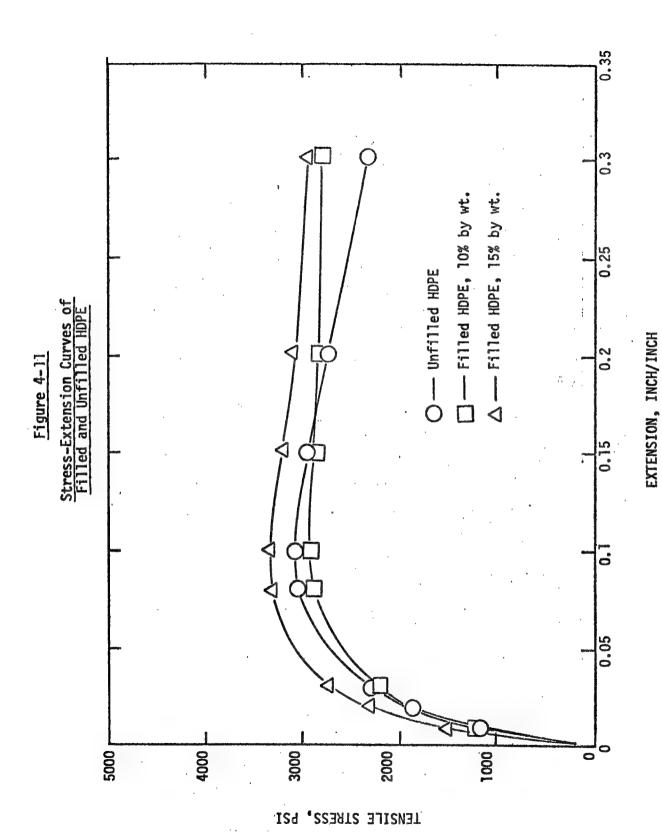


Figure 4-10

Isochronous Stress-Modulus Curves of Polybutylene



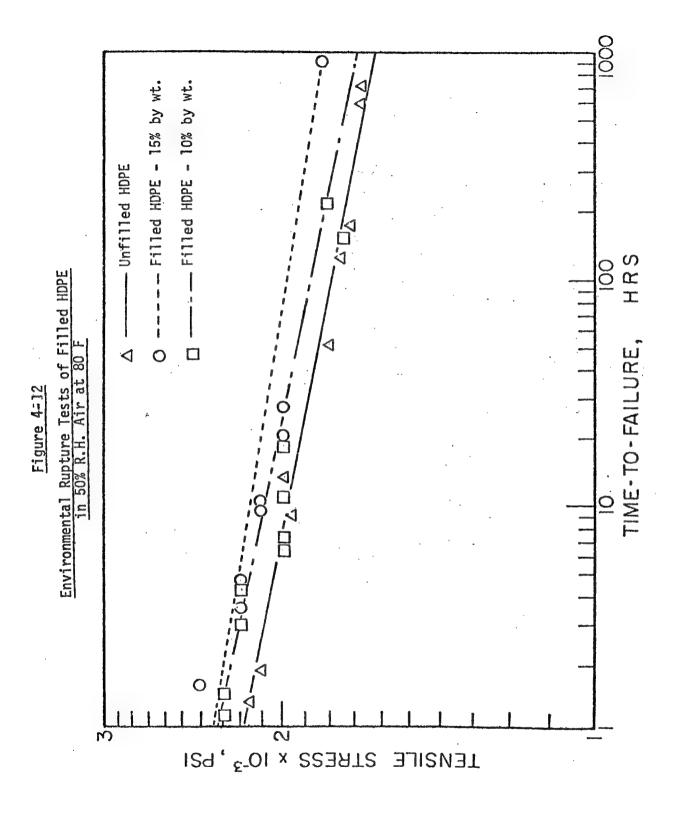
TENSILE STRESS, PSI



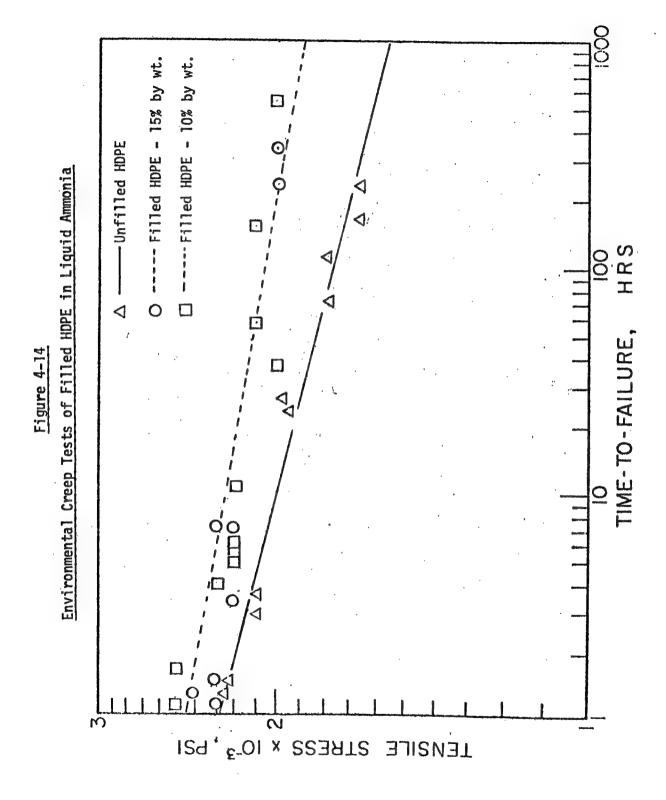
through 196. The designation code for HDPE compounded with 10 and 15 percent by weight acetylene black are PDX-77373 and PDX-77372 respectively.

The environmental rupture tests were also repeated for the compound materials. Tensile stress versus time-to-failure curves for PDX-77372 and PDX-77373 in different environments are shown in Figures 4-12, 4-13 and 4-14. For comparison purpose, the experimental data of unfilled HDPE are also included in these figures. The creep strain vs. time curves for these two compounded HDPE are presented in Figures 4-15 and 4-16. The coefficients of Kinney's equation for these compounds are listed in Table 4-2. Isochronus stress-modulus curves calculated from Kinney's equations for PDX-77372 and PDX-77373 are plotted in Figures 4-17 and 4-18 respectively.

These results indicate that the filler does not dramatically influence the loading-ability of HDPE. The mechanical performance of these compounds may be as satisfactory as HDPE.



---Filled HDPE - 15% by wt. -Filled HDPE - 10% by wt. -Unfilled HDPE Environmental Creep Tests of Filled HDPE in Seawater HRS 4 TIME-TO-FAILURE, Figure 4-13 0 0 8 STRESS x 10<sup>-3</sup>, PSI **LENSIFE** 



Creep Strain Curves of HDPE Compounded with 10% Acetylene Black by Weight

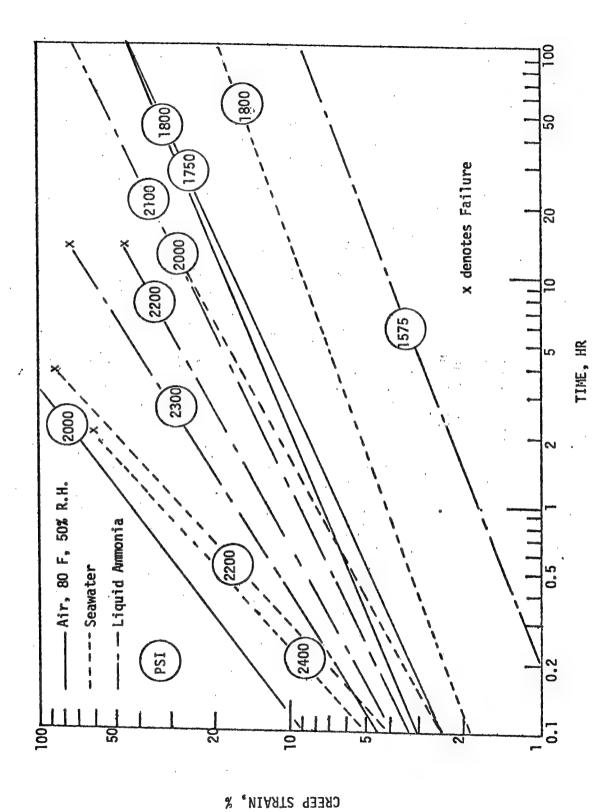
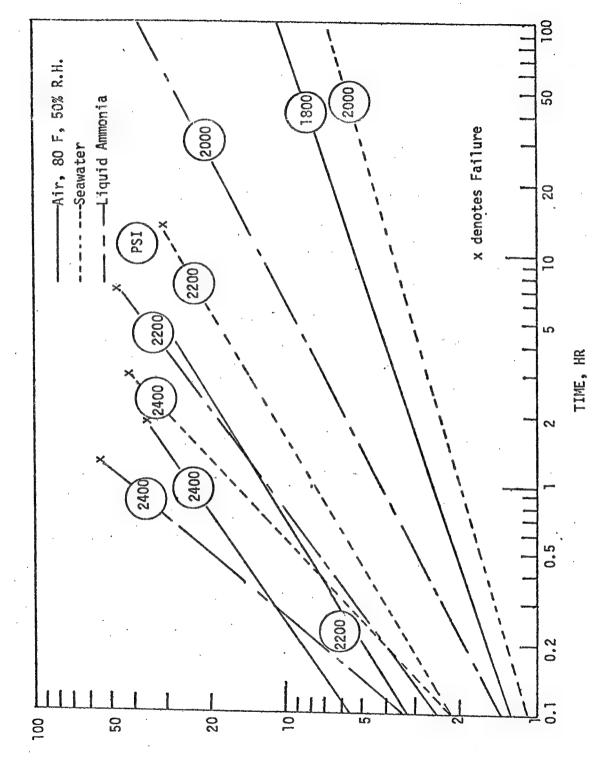


Figure 4-16

Creep Strain Curves of HDPE Compounded with 15% Acetylene Black by Weight



CREEP STRAIN, %

Table 4-2

Coefficients of Kinney's Equation for Filled HDPE

**************************************			CONSTANTS IN KINNEY CREEP MODULUS EQUATION	
SYSIEM	STRESS	≪	B	ပါ
AIR - PDX-77372	1800 2000 2200 2400	7.5651 × 10 <sup>4</sup> 4.8967 × 10 <sup>4</sup> 3.1854 × 10 <sup>4</sup> 2.0170 × 10 <sup>4</sup>	2231 x 1 6846 x 1 9959 x 1 9342 x 1	-3.6548 x 10 <sup>-1</sup> -1.6450 x ·10 <sup>-1</sup> -5.6291 x 10 <sup>-2</sup> -2.2434 x 10 <sup>-1</sup>
NH - PDX-77372	2000 2200 2300 2400	< ××××	× ××××	× ××××
SEAWATER - PDX-77372	1800 2000 2200 2400	4.3875 × 10 <sup>4</sup> 1.0057 × 10 <sup>5</sup> 3.1586 × 10 <sup>4</sup> 2.1529 × 10 <sup>4</sup>		××××
AIR - PDX 77373	1750 1800 2000 2200 2300	2.8504 × 10 <sup>4</sup> 2.6278 × 10 <sup>4</sup> 4.9725 × 10 <sup>3</sup> 1.2468 × 10 <sup>4</sup> 3.0305 × 10 <sup>3</sup>	-1.2656 × 10 <sup>4</sup> -1.2087 × 10 <sup>4</sup> -2.3687 × 10 <sup>4</sup> -3.5004 × 10 <sup>4</sup> -5.7190 × 10 <sup>4</sup>	3355 x 1 7397 x 1 9813 x 1 6043 x 1
NH -PDX-77373	1575 2000 2100 2200 2300	1.0911 × 10 <sup>5</sup> 1.9445 × 10 <sup>4</sup> 2.4463 × 10 <sup>4</sup> 1.9254 × 10 <sup>4</sup> 1.1836 × 10 <sup>4</sup>	0230 × 1 0304 × 1 2238 × 1 0829 × 1 6911 × 1	.0951 x .878 x .6431 x .8758 x
SEAWATER - PDX-77373	2000 2200 2400 1800	2.7819 x 10 <sup>4</sup> 1.0287 x 10 <sup>4</sup> 6.8332 x 10 <sup>4</sup> 4.9776 x 10 <sup>4</sup>	-2.3977 × 10* -2.5140 × 10* -2.0319 × 10* -1.2609 × 10*	-3.2942 × 10 <sup>-1</sup> -1.2649 × 10 <sup>-1</sup> -3.1595 × 10 <sup>-1</sup> -3.5331 × 10 <sup>-1</sup>

Figure 4-17
Isochronous Stress-Modulus Curves of HDPE
Compounded 15% Acetylene Black by Weight

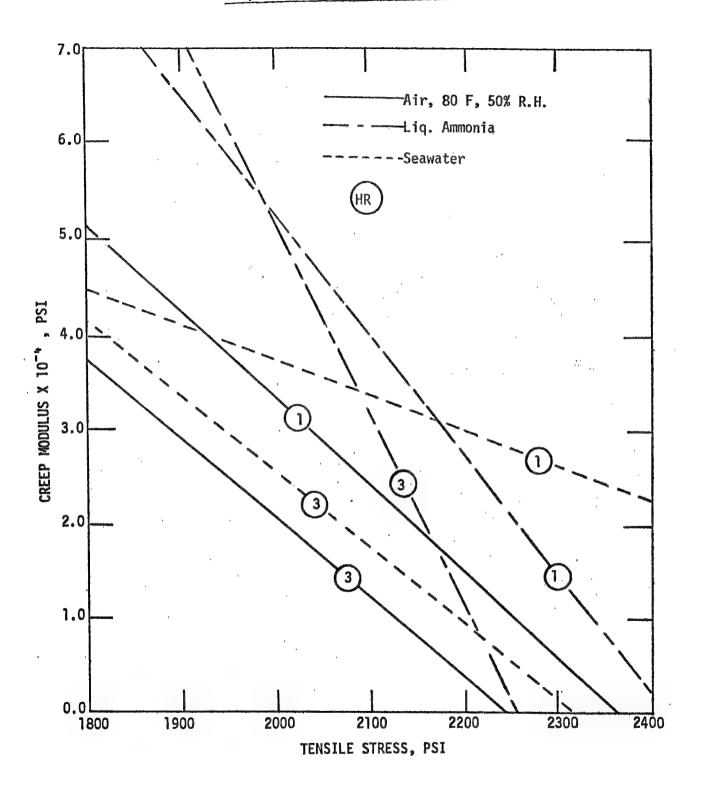
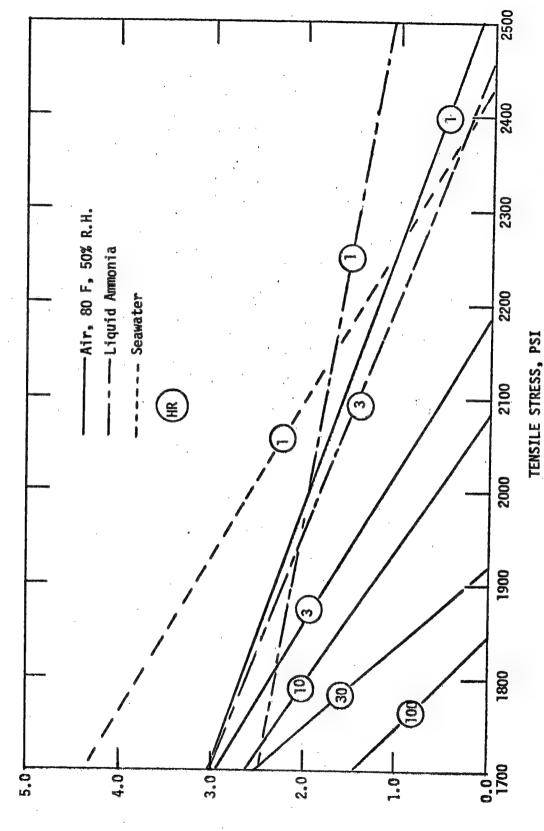


Figure 4-18

Isochronous Stress-Modulus Curves of HDPE Compounded 10% Acetylene Black by Weight



CKEEP MODULUS x 10 ... PSI

## SECTION 5

## THERMAL CONDUCTIVITY

## 5.1 GENERAL

As previously mentioned, low thermal conductivity of plastics is one of the major disadvantages of plastic heat exchangers. The thermal conductivity of solid plastic material depends on the crystallinity of the material and the previous thermal history. HDPE has the highest thermal conductivity of all commercial available thermoplastics. Usually, the thermal conductivity of metal is 2 or 3 orders of magnitude higher than that of HDPE. However, solid fillers are often added to thermoplastics to obtain composite materials with improved physical properties.

In this study, acetylene black is selected as a filler material because it exhibits favorable mechanical properties, such as lower elongation and higher modulus. The thermal conductivity of acetylene black particles has not been measured because of their small size (425 A). However, acetylene black has been used in rubber to increase thermal and electrical conductivity. A series of thermal conductivity measurements of HDPE compounded with 10% and 15% by weight acetylene black filler were performed. A method has been developed to predict the thermal conductivity at higher filler composition.

## 5.2 EXPERIMENTAL

The coefficient of thermal conductivity was measured using a Cenco-Fitch apparatus, which consists of a constant heat source, a receiver and a potentiometer. The heat source is an insulated copper vessel with a nickel plated bottom and is maintained at constant temperature by circulating water from a constant temperature bath. The receiver is an insulated copper plug with a heat capacity of 0.093 cal/gm- C. Both the heat source and the receiver have copper/constantan thermocouples embedded in them. The potentiometer is connected to the copper terminals, and a piece of constantan is connected between two constantan terminals. Therefore, the temperature difference between heat source and receiver is measured by the potentiometer.

Each test was started by stabilizing a circulating water bath at the desired temperature. The receiver was always at room temperature initially and the source at some higher temperature maintained by the bath. The specimen, which was 3 inches square injection molded sheet of material approximately 1/8 inch thick, was placed on a large aluminum slab and heat source. This aluminum slab served as temperature sink to establish a linear gradient in the specimen. A 5 kg weight was put on the source vessel to insure exclusion of air from the surface. After about 5 minutes, the specimen and heat source were placed on the receiver. Potentiometer readings were taken at every 3-minute interval until a total of at least 15 readings were reached. These potentiometer readings represent the temperature difference between the heat source and the receiver.

Since the value of thermal conductivity of copper is much greater than that of plastic, the heat transfer resistance of copper in the Cenco-

Fitch equipment is assumed to be negligible. Furthermore, the temperature gradient inside the specimen is assumed to be linear. The following expression may be used to determine the thermal conductivity:

$$k = \frac{1MC(1n\Delta T_0 - 1n\Delta T_t)}{At}$$
 (5-1)

where

A = specimen cross section area

C = receiver specific test

1 = specimen thickness

M = receiver mass

t = elapse time

 $\Delta T_0$  = temperature difference between source and receiver

at time 0

 $\Delta T_t$  = temperature difference between source and reciever at time t

# 5.3 RESULTS AND DISCUSSION

Figure 5-1 shows thermal conductivity of the unfilled and filled HDPE versus temperature, which is the average temperature between the heat source and the receiver.

Thermal conductivity in polyethylene is sensitive to density which is related to the degree of crystallinity. The measured thermal conductivity of the unfilled resin with a density of 0.945 gm/cl is in good agreement with other published data  $^6$  for polyethylene of similar density.

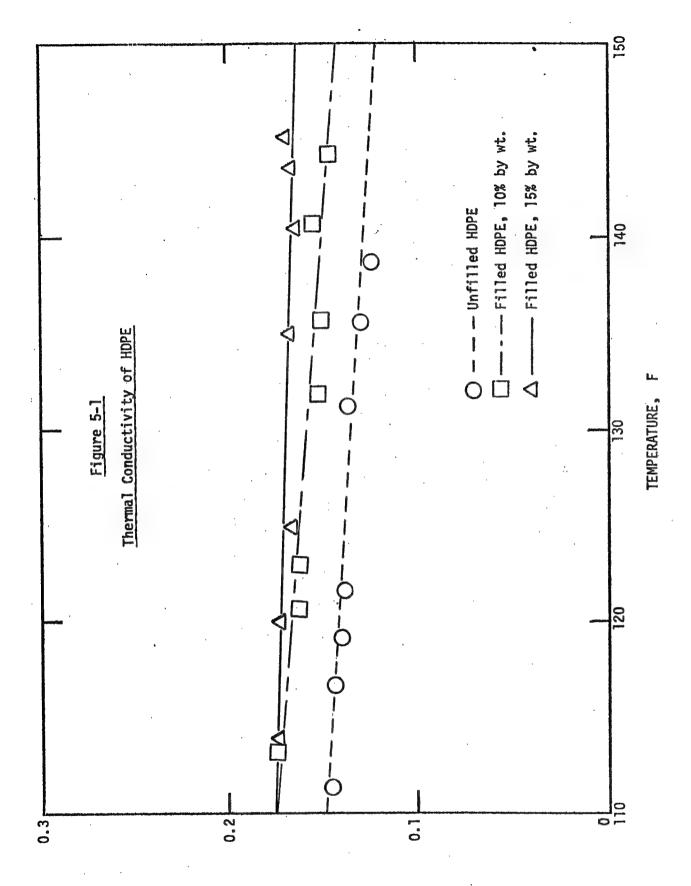
Many theoretical and empirical models, such as Maxwell equation<sup>18</sup>, Beherens-Peterson-Hermans equation; and Cheng-Vachon equation; have been proposed to predict thermal conductivity of two phase mixture. Among all of the equations the Maxwell equation is relatively simple and fairly accurate at low volume fraction. Maxwell used potential theory to derive an equation for electrical conductivity of randomly distributed discreet particles in a continuous phase. This equation has been experimentally proved to be valid for thermal conductivity of a two phase mixture.

The expression of of this equation is:

$$k_{e} = k_{c} \frac{2\phi k_{c} + (3-2\phi)k_{d}}{(3-\phi)k_{c} + \phi k_{d}}$$
 (5-2)

where

kc = thermal conductivity of continuous phase
kd = thermal conductivity of discrete phase
ke = thermal conductivity of two phase mixture
ø = volume fraction of discrete phase



THERMAL CONDUCTIVITY, BTU/HR-T-T-F

Eq (5-2) may be rearranged as

 $\frac{k_d}{K_C} = \frac{2\phi k_C - 3k_e + \phi k_e}{2\phi k_C - 3k_C + \phi k_e}$ 

(5-3)

It is important to note that the thermal conductivity of the discrete phase, i.e., acetylene black, is unknown. However, the ratio,  $kd/k_{\text{C}},$  in Eq. (5-3) can be obtained from the experimental data of HDPE compounded with 10% and 15% by weight acetylene black filler as shown in Figure 5-1. Within a narrow temperature range, this ratio may be treated as a constant and is used to predict thermal conductivity of any HDPE compound of higher composition without serious error.

Once  $(k_{\rm d}/k_{\rm C})$  is determined, the  $k_{\rm C}$  in Eq. (5-3) can be calculated for a given value of volume fraction or weight percentage of the discrete phase.

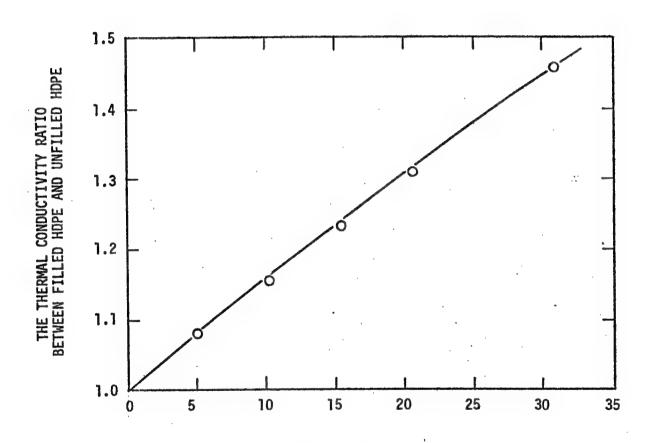
Figure 5-2 shows that the thermal conductivity ratio between HDPE filled with acetylene black and unfilled HDPE is plotted against the weight percentage of the filler material. This should be considered the upper limit for acetylene black. It is interesting to note that the thermal conductivity may be enhanced 50% by compounding the HDPE with 34% by weight acetylene black.

The improvement in conductivity of the filled materials was less than expected based on data for filled rubber. It is possible that the sensitivity of conductive blacks to "over-compounding", i.e., excessive shear during blending, resulted in lower conductivity. The loadings obtained were relatively low because the low bulk density of the carbon black made it difficult to compound. Tensile tests have indicated that it may be possible to use a higher percentage by weight of filler without adversely affecting mechanical properties. Other fillers such as atomized aluminum, carbon microballons, and mineral powders may be recommended for future testing.

Figure 5-2

Relationship between HDPE Thermal Conductivity and Weight

Percentage of Acetylene Black



WEIGHT PERCENTAGE OF ACETYLENE BLACK, %

#### SECTION 6

#### PERMEABILITY TESTS

#### 6.1 GENERAL

Since plastics are low density material in consequence of their relatively loose structure, they are not a very effective barrier to the transmission of ammonia or water. A plastic heat exchanger in OTEC would allow a small but undesirable amount of mixing of the two fluids. Since water transmission rates are published for virtually all types of commercial plastics only the permeation rate of ammonia requires experimental determination.

Permeation occurs in the following consecutive steps: 1) solution in the plastic, 2) diffusion, and 3) dissolution at the opposite surface. The permeability coefficient is therefore a product of the diffusion constant and solubility coefficient both of which depend on numerous variables, such as:

- 1) Nature of the plastic materials
- 2) Nature of the test fluid
- 3) Concentration or partial pressure of the test fluid
- 4) Temperature
- 5) Time of permeation
- 6) Thickness of plastics material

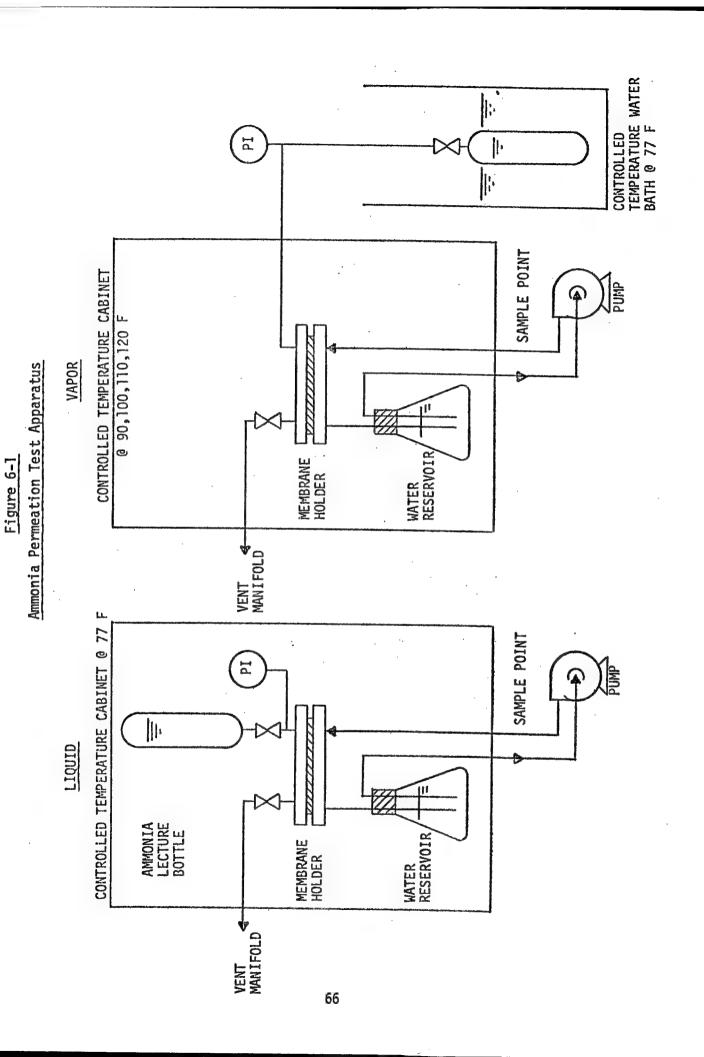
For our application however, the rates of transmission of ammonia and water under specific conditions are of more interest than the mechanisms. Thus, the scope of this study is limited to the determination of the permeability of ammonia to unfilled and filled HDPE and possible coating or surface treatment which may be a barrier to ammonia.

The temperature influence on ammonia permeability through HDPE is also investigated. This will allow accurate calculation of permeation rate at any temperature of interest.

#### 6.2 EXPERIMENTAL APPARATUS

A test which simulates OTEC conditions was suggested by the relative ease of measuring small concentrations of ammonia in water. Figure 6-1 is a schematic of the apparatus used to measure the permeability of ammonia liquor or vapor through a plastic membrane interposed between ammonia and circulating distilled water. Since permeation through non-porous membranes occurs by the consecutive steps of solution of a permeant in the polymer and diffusion of the dissolved permeant, the presence of water on the low pressure side of the membrane may influence permeability because of the high solubility of ammonia in water and possible reaction of water and ammonia inside the plastic.

The apparatus consisted of a 142 mm stainless steel filter holder (Millipore Cat.No. YY22 142 30) in which the test specimens were mounted. Anhydrous ammonia liquid or vapor was supplied to the high pressure side of the specimen from a small cylinder which was either placed in a cabinet with membrane cell or in an external water bath. Both cabinet and water bath can be maintained at constant temperature. The distilled water was



circulated through the low pressure side of the membrane cell and a 500 ml flask as a water reservoir by a seal-less, magnetically driven pump.

Ammonia diffusing through the plastic specimens was dissolved into distilled water. The solubility of ammonia in water is very high at room temperature and the amount of ammonia diffusing through the specimen is very small. Therefore, it is assumed that the ammonia is completely dissolved in the water. The concentration of ammonia in water can be measured by an ammonia electrode (Orion model 95-10) and a specific ion meter (Orion Model 407A).

# 6.3 PROCEDURES

The testing specimen was first mounted to the filter holder, which was placed inside a temperature controlled cabinet. The water reservoir was filled with 500 ml distilled water which was circulated through the filter holder by a pump. Then the ammonia was supplied to the high pressure side of the filter holder. Another flask containing 500 ml distilled water was placed inside the cabinet for later use. The whole system was stabilized at a desired temperature for 12 hours. Since some of the specimens were as thick as 1/8 inch, this step also allows the specimen to establish a steady-state ammonia diffusion process. When the 12-hour precondition period was over, the circulated water solution, which now contained ammonia, was drained out completely. The system was then refilled with clean distilled water from the standby 500 ml flash which had previously been placed in the cabinet to reach the proper temperature.

During the tests, small samples (6 ml) of solution were withdrawn at 30-minute intervals until a total of at least 10 readings were reached. The ammonia concentration of this solution was measured using an ammonia electrode and specific ion meter immediately after sampling. From these concentration measurements, the total amount of ammonia permeating through the specimen was calculated.

# 6.4 RESULTS AND DISCUSSION

The results of these tests are expressed in terms of permeability coefficient P, i.e.

The conventional unit of P is  $(cm^3 (STP) cm cm^{-2}Sec^{-1}(cm Hg)^{-1})$ .

The temperature dependence of the permeability coefficient is represented by the following Anhenius relation<sup>23</sup>.

$$P = Po exp (-Ep/RT)$$
 (6-2)

Where: Po = constant

Ep = the activation energy of permeation, KJ/mole

R =the gas constant (8.3144 J/K°-mole)

T = the absolute temperature, "K

A typical set of permeation data of liquid ammonia through HDPE (F364 Soltex), is shown in Figure 6-2. The increasing slope during the first three hours is characteristic of the time required for ammonia molecules to diffuse through a relatively thick plastic wall (0.116 inch). A permeability of  $1.4723 \times 10^{-9} \text{ cm}^3$  (STP) cm cm<sup>-2</sup> sec<sup>-1</sup>(cm Hg)<sup>1</sup>at 77 F was calculated from the slope of the curve between 3 and 8 hours and specimen area (158.4 cm), thickness and pressure difference across the specimen (145.4 psi). The positive intercept of the curve is probably a combined effect of reduced ion meter accuracy at very low ammonia concentrations and the residual ammonia present in the distilled water used for the test. The average permeation coefficient of liquid ammonia through Soltex F364 at 77 F, determined from three independent tests, is  $1.74 \times 10^{-9}$ .

A series of tests were also run with ammonia vapor on F364 at temperatures ranging from 77 F to 120 F in order to assess the temperature dependence of the permeation rate and determine whether the liquid permeates faster than the vapor. Results are presented in Figure 6-3.

The permeation coefficients obtained from Figure 6-3 have been plotted against inverse absolute temperature in Figure 6-4. According to Arrhenius equation (EQ. 6-2), the slope of this curve represents the permeation activation energy, i.e. 35.2 KJ/mole. This value is obtained from the least-squares fitting of the data in Figure 6-4. The ammonia transmission rate increases about 3% for every degree Fahrenheit increase in temperature. Figure 6-4 also indicates that the rate of vapor permeation at 77 F is roughly half that of the saturated liquid at the same temperature and vapor pressure.

The ammonia permeabilities of HDPE compounded with 15% by weight acetylene black determined from two independent tests is 1.76  $\times$  10<sup>-9</sup>cm (STP) cm<sup>3</sup> cm<sup>2</sup> sec<sup>-1</sup> (cm Hg)<sup>71</sup> at 77 F which is within experimental accuracy of the value for unfilled HDPE, i.e. 1.74  $\times$  10<sup>-9</sup>.

These tests are aimed at reducing the rate at which ammonia permeates through walls of the PHX. This rate has been quantified for unmodified HDPE by the experiments described above. For a heat exchanger using a 26 mil wall profile, which is shown in Figure 6-5, as the core test unit, the ammonia loss would amount to 0.0009 lbs/day/sq ft of heat transfer surface at 50 F. In more general terms, based on calculated condenser core test unit performance, this is a loss of 0.41 lb/l0 6 Btu/F. It is interesting to note that this figure will be almost independent of thickness for relatively heavy walls because of the proportionality of thermal and permeation resistance of the wall.

It is important to put this ammonia loss into perspective and to compare it to ordinary leakage. One conceptual 25 MWe OTEC module has a sea water flow through the condenser of 7551 cfs and a heat load of 1,020,443 Btu/sec at an LMTD of 8 F  $^{2+}$ . If the permeation loss figure is applied to a PHX having the same duty, the ammonia concentration in the condenser cooling water discharge would be 0.1 mg/l. This is 25% of the EPA limit for ammonia concentration in marine water $^{25}$ . For comparison, the leakage rate of this 25 MWe aluminum shell-and-tube condenser can be roughtly estimated. For instance, some of the largest shell-and-tube "heat exchangers"

Figure 6-2

A Typical Permeation Data of Liquid

Ammonia through HDPE

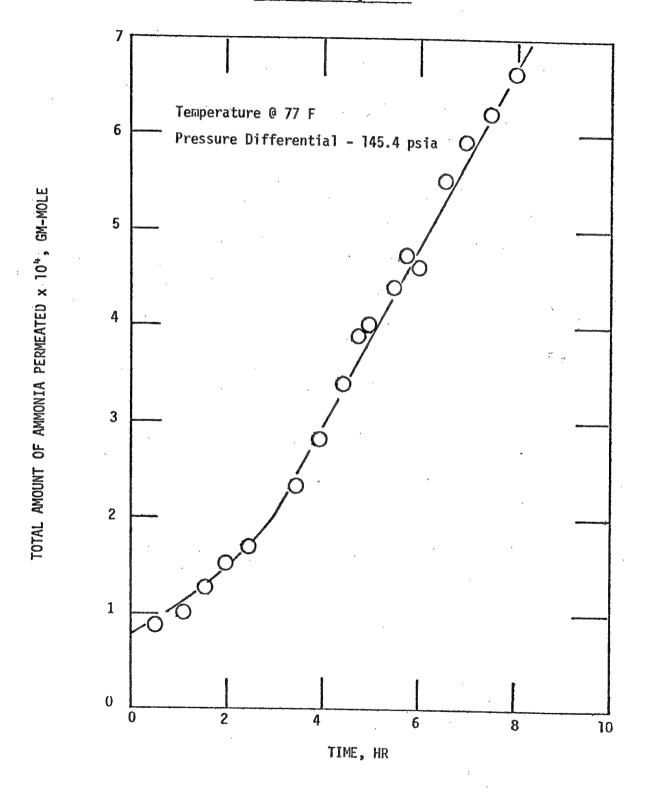


Figure 6-3

Animonia Vapor Transmission through HDPE

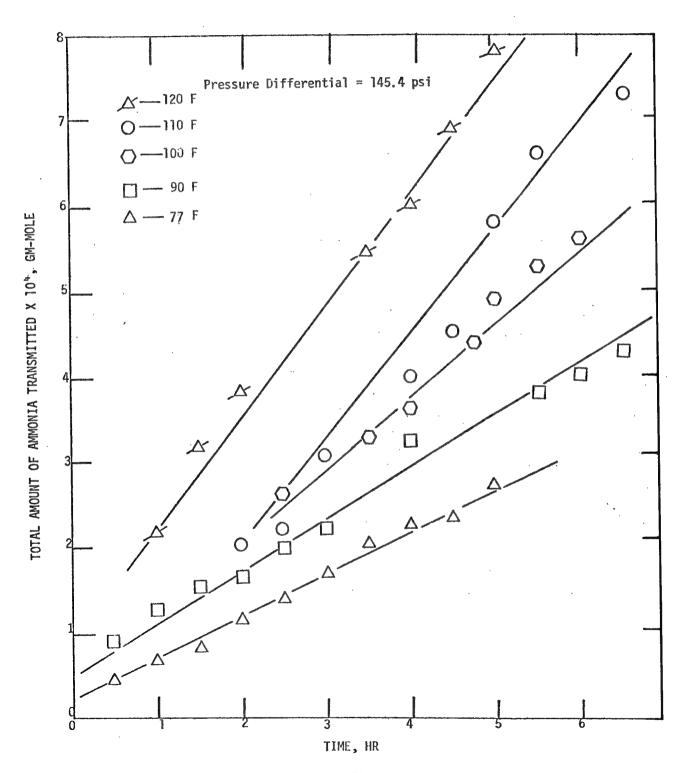


Figure 6-4

Temperature Dependence of Permeability

Coefficients for Ammonia Vapor through HDPE

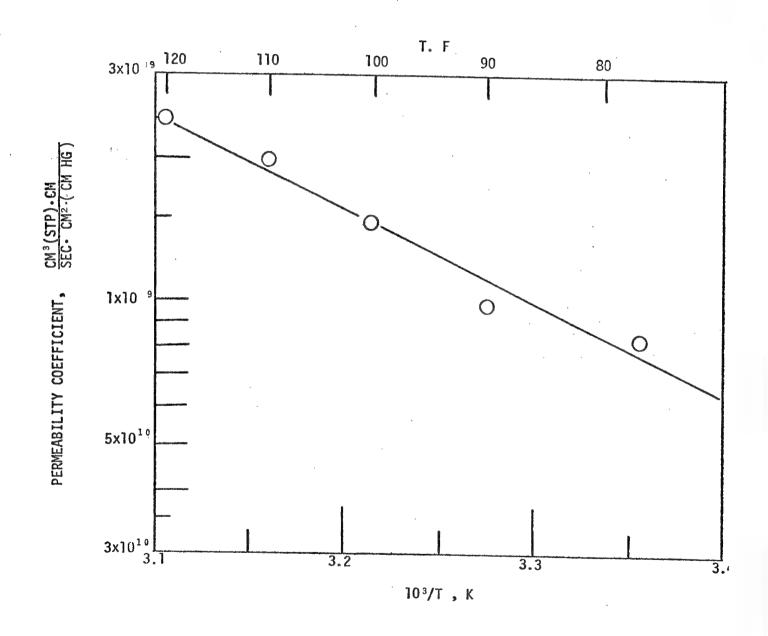
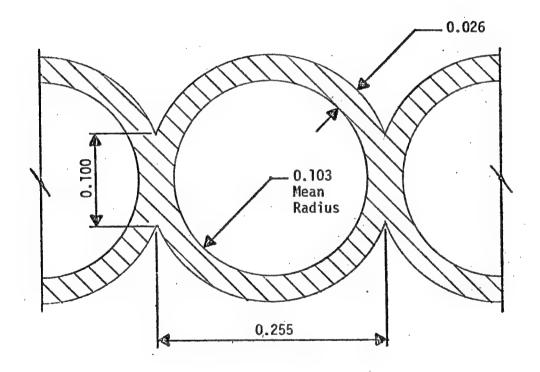


Figure 6-5
Nominal Profile Cross Section Dimensions



in existence are sea water evaporators. Oak Ridge National Laboratory (ORNL) estimated the minimum air inleakage rate attainable for a conceptual 50 MGD desalting module under vacuum at 8.33 lb/hr which amounted to 0.0487 lbs/hr per 100 ft of seal weld for that plant<sup>26</sup>. If this rate is applied to the tube-to-tubesheet welds of the 25 MWe aluminum condenser and related to ammonia gas leakage through an equivalent orifice with a 75 psi differential, an ammonia concentration in sea water of about 0.1 mg/l would result; this is the same concentration calculated for the PHX. The ORNL figure is probably optimistic since actual inleakage rates measured for evaporators have been orders of magnitude greater.

Regardlness of its source, it appears that the most objectionable consequence of working fluid loss is the additional cost of power it represents. Therefore, several barrier materials were tested in an effort to reduce permeation losses. At first, the coextrusion of composite films was suggested to approach the ammonia barrier problem. A lamination of 0.5 mil aluminized polyester to a 2.2 mil coextruded HDPE film (ALURE CX. St. Regis) were tested. The HDPE side was exposed to liquid ammonia since HDPE has high chemical resistance to ammonia. The unfavorable result of the polyester film being dissolved, was observed. Another type of coextrusion films, a 0.6 mil aluminized nylon laminated to a 2.5 mil EVA low density polyethylene (LDPE) substrate (ALURE N, St. Regis) was also tested. In this case, the more resistant side of the film, i.e. nylon, was faced to the ammonia side of the transmission cell. The polyester adhesive between the nylon and polyethylene dissolved. The metalized film definitely has a desirable barrier property. However, a film combination which does not include polyester is required for use with ammonia.

Experiments of barrier performance of an epoxy coating against ammonia permeation were performed. Only one type of epoxy coating (Unicoat 33, Amicon) was tested. A 2 mils thick, low density polyethylene (LDPE) film of a measured ammonia permeability was coated by Unicoat 33 with a thickness of 5 mills. This epoxy coating separated from LDPE film after exposure to liquid ammonia and dissolved in the ammonia to form a white solid. When long-term durability test specimens were fabricated, several different types of epoxy were used to bond the HDPE. These were tested in liquid ammonia. Although a number of these were represented as being resistant to ammonia, all have proved unsuitable because of swelling and cracking after only a few days exposure. In conclusion, epoxy may not be a reliable barrier material against ammonia.

Another type coated material, saran-coated polypropylene film (Type CB500/25, Hercules), was tested for the ammonia barrier property. This polypropylene film, with a thickness of 0.51 mil, is coated with a 0.25 mil of saran on both sides. The average permeation coefficient of ammonia liquid through saran-coated polypropylene from two independent tests at 77 F is 1.086 x  $10^{-9}$ cm (STP) cm cm<sup>-2</sup> Sec<sup>-1</sup>(cm Hg)<sup>-1</sup> which is close to the reported value of ammonia vapor permeability through polypropylene, i.e. 9.2 x  $10^{-10}$  . A change of this water-colored film to brownish color was observed. This indicated that there is a possible chemical reaction between saran coat and ammonia and therefore, unacceptable as an ammonia barrier coating.

Two types of gas phase treatment, i.e. sulfonation and fluorination, have shown tremendous improvement in reducing gasoline permeation through the

HDPE tank. The sulfonation process, which was developed by Dow Chemical Company, attaches SO3 and NH3 ions to the plastic. Some permeation tests of sulfonated HDPE were performed. Results of treated HDPE are summarized and compared with untreated HDPE as follows:

Permeability
<a href="mailto:cm3">cm3 (STP)</a> cm
<a href="mailto:cm7">cm2</a>sec - (cmHg)

<u>Plastic</u>

Untreated F364

1.744 x 10<sup>-9</sup>

Two side sulfonated F364

0.992 x 10<sup>-9</sup>

This indicates that the permeation of ammonia has been reduced about 43% for the sulfonated F364. It is interesting to note that the surface of the above sulfonated HDPE specimen was probably treated to a depth of several modecular layers, i.e. I mil roughly. Therefore, the ammonia loss of a double-side sulfonation treated 10 mil thick HDPE surface would be reduced by 86% as compared to an untreated surface.

The fluorination process was originally developed by Air Products. Their reports<sup>27</sup> suggests that fluorination treatment is very effective for permeants with solubility parameters below 9.0 or above 10.0. The data of permeation vs. permeant solubility parameter suggests that this process could be very effective for ammonia barrier purposes, since the solubility parameter of ammonia is 16.3 Unfortunately, the samples of fluorinated HDPE were unattainable at the time of writing this report. The determination of effectiveness of fluorinating HDPE to reduce the rate of ammonia transmission is recommended for further test.

#### SECTION 7

#### LONG TERM DURABILITY TESTS

### 7.1 GENERAL

In the successful design of load-bearing plastic components, a knowledge of strength is as important as an understanding of deformational behavior. The knowledge of strength can be classified into two major problems, i.e., resistance to impact and the ability to withstand sustained loads. The former can be dealt with by short term tests, such as the chemical resistance tests and environmental rupture tests discussed in previous sections. The latter can be confirmed by the long term durability tests presented in this section.

The long term durability tests are aimed at producing information about allowable working stress in a simulated OTEC environment that is directly applicable to the design of HDPE heat exchangers. These tests differ from the environment rupture tests in several respects. The environment rupture tests involved tensile specimens simulatneously exposed to a uniform environment (liquid ammonia, sea water or air) and uniaxial tensile stress for a nominal maximum period of 300 hours. Most significantly, the nominal duration of long term durability tests is approximately 3000 hours, an order of magnitude increase over the environment rupture tests.

# 7.2 EXPERIMENTAL

ASTM D1598 $^2$ 8 was used as a guideline to develop the apparatus and testing procedures. Long term durability test specimens were sections of HDPE heat exchanger panel and were mounted as shown in Figure 7-1. The dimension of nominal profile cross section is presented in Figure 6-5.

The material of this heat exchanger panel is the same type HDPE resin (F364, Soltex) used for previous tests. Each end of a  $5\frac{1}{2}$  inch long panel, consisting of three tubes, was welded to a HDPE disc by hot plate welding. This hot plate welding method provided not only a leak free seal but also a strong bond which can sustain the testing pressure for these heat exchanger panels. The discs served as tube plates and were clamped between two flanges.

The assembled testing specimen was then placed inside a chamber consisting of a section of three inch schedule 40 aluminum pipe 13.5 inches long with end caps secured by Victaulic couplings. The specimen was internally filled with anhydrous ammonia liquid which was furnished from an ammonia reservoir. The ammonia reservoir had the same set-up as the specimen chamber. The chamber, outside the specimen, was full of sea water at atmosphere pressure. Both the specimen chamber and ammonia reservoir were immersed in a constant temperature bath.

An electric clock was installed in order to monitor the failure time of the specimen. A pressure switch was connected directly to the specimen chamber, not to the specimen itself. When the specimen failed, the

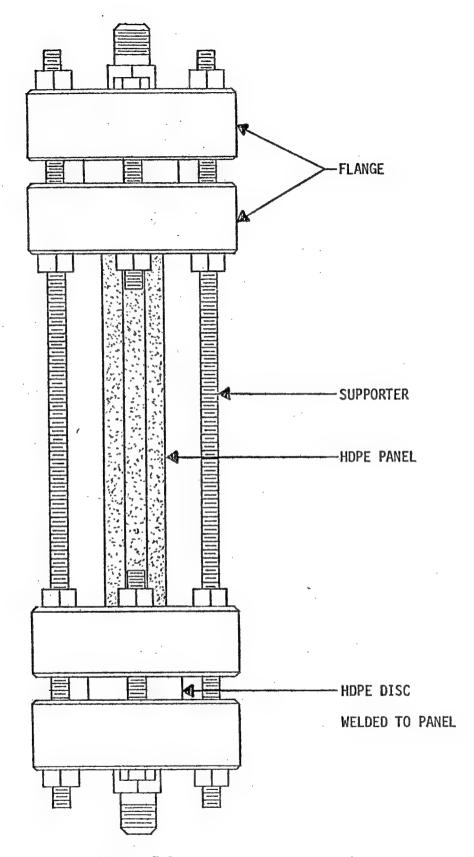


Figure 7-1
Specimen for Long Term Durability Tests

ammonia side of the specimen released pressure. For any pressure higher than 30 psia, the pressure switch de-energized the clock. Six long term durability test stations were installed in the constant temperature bath. schematic of the apparatus is shown in Drawing No. 059-7108.

Since specimen were placed in a simulated OTEC environment, preconditioning was not necessary. Both the specimen and ammonia reservoir can be pressurized by nitrogen to the desired pressure. The sea water inside the specimen chamber was replaced every day during the testing period because of the possible formation of scale.

The environmental rupture tests indicated that there is considerable scatter in specimen life for each stress. For this reason, five specimens were tested at each stress level allowing the probability of failure to be introduced and related to time and stress.

#### 7.3 RESULTS AND DISCUSSION

The definition of failure can be expressed as any continuous loss of pressure resulting from the transmission of the test liquid through the body of the specimen under test. Generally, the failure of the plastic pipe or tube may be classified as ballooning, bursting and seepage or weeping, which are defined in ASTM D1598. <sup>28</sup> A photograph of a failed specimen is shown in Figure 7-2 and indicates that the failure is ballooning type because of the abnormal localized expansion.

The long term durability test data are plotted as hoop stress versus time-to-failure in Figure 7-3. By definition, the hoop stress can be expressed as follows:

$$S = p(D-t)/2t \tag{7-1}$$

#### where:

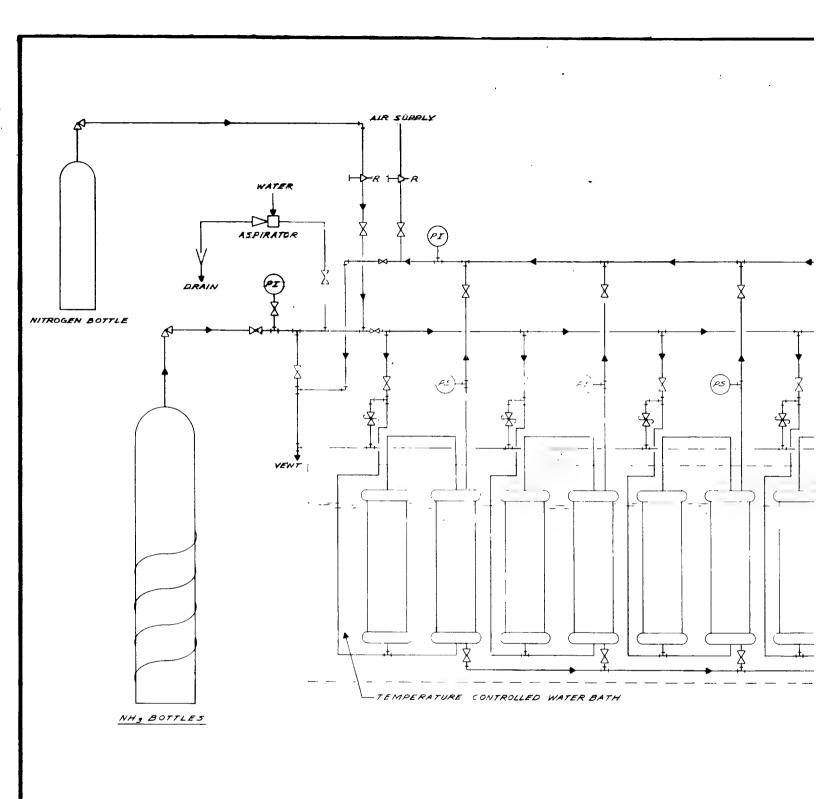
S = hoop stress, psi

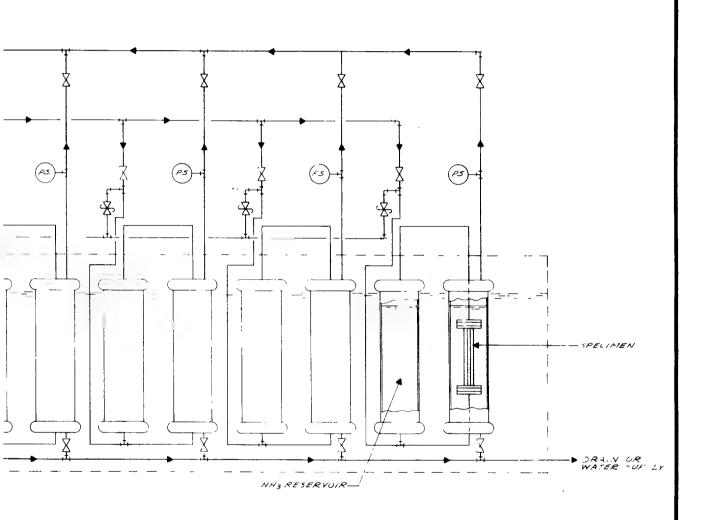
P = internal pressure, psi

D = average outside diameter, inch

t = minimum wall thickness, inch

These data are also listed in Table 7-1. It is important to note that after being at test conditions for over 3000 hours, some of the specimens did not fail. Ogorkiewicz<sup>29</sup> has suggested that the extrapolation in time from stress vs. time-to-failure curves by a factor of ten is considered to be the upper limit. Hydrostatic tests lasting 30,000 hours would provide estimates for a life of 3.5 years, still short of the design life of an OTEC heat exchanger. However, there would seem to be little justification for tests of 10,000 hours at the present stage of development under the following circumstances. The HDPE pipe has already been subject to hydrostatic failure tests of at least 10,000 hours in accordance with ASTM D2837<sup>28</sup> by Whyman and Szpak<sup>30</sup> The failure data points are also shown in Figure 7-3. It appears that they are in good agreement with the data reported here. Therefore, the failure characteristics for the long term durability tests of this report do not differ significantly from established behavior. If no "knee" occurs in the hoop stress vs.





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APPROVALS

MEDICAL COMMENTS

APPROVALS

MACHINE PS. 177-77

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Figure 7-2
Failed Long Term Durability Specimen

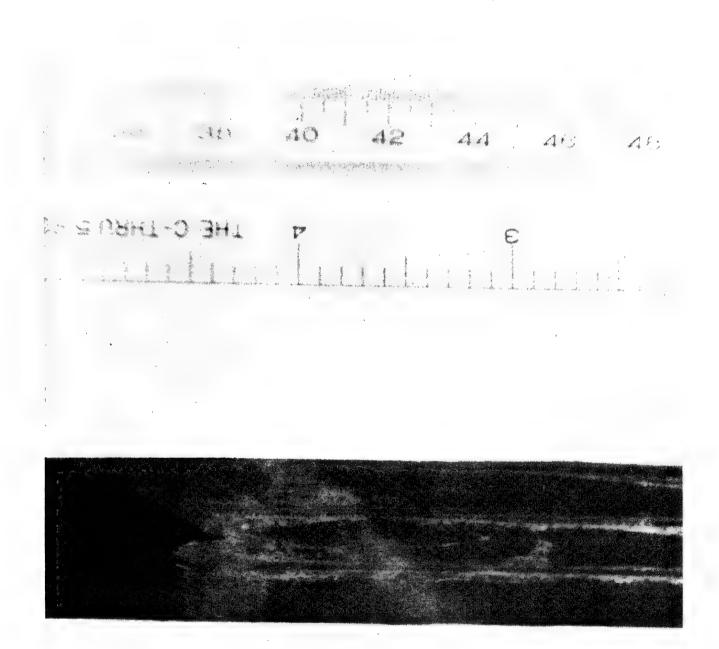
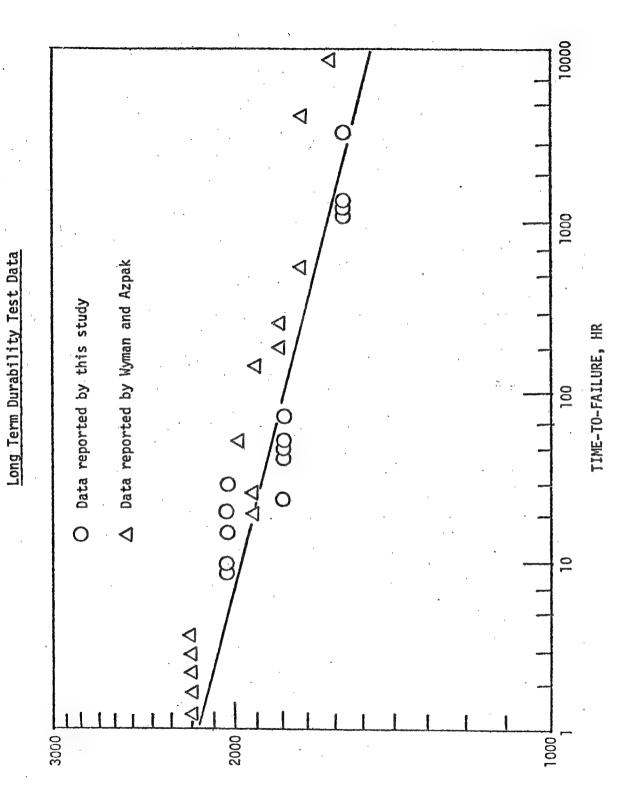


Figure 7-3



HOOP STRESS, PSI

Table 7-1
Long Term Durability Test Data

TEST NO	HOOP STRESS (PSI)	TESTING TIME (HRS)	FAILURE
01	1785	77.07	YES
02	1785	51.05	YES
03	1785	23.87	YES
04	1785	50.63	YES
05	1785	42.93	YES
06	2010	14.00	YES
07	2010	8.22	YES
08	2010	8.62	YES
09	2010	27.367	YÉS
10	2010	19.850	YES
11	1560	1369.50	YES
12	1560	1275.28	YES
13	. 1560	3192.00	NO
14	1340	2688.00	NO
15	1340	2664.00	NO
16	1340	2664.00	NO
17	1340	2040.00	NO
18	1560	1128.00	NO

time-to-failure curve caused by the onset of static fatigue or environmental stress cracking, the material will probably continue to display typical linear behavior until 10,000 hours.

It was found that deposits formed on surfaces of the long term durability test specimens after immersion in sea water for only a few days. In this case, the sea water was stagnant and an appreciable concentration of ammonia hydroxide built up. Although the deposits were not analyzed they dissolved immediately in a dulute acid solution.

Although the bulk concentration of ammonium hydroxide in sea water caused by ammonia permeation would be very small, the possibility of calcareous deposit formation on the plastic surface exits. An analogy with impressed current cathodic protection can be drawn to estimate the likelihood of calcium carbonate and magnesium hydroxide precipitation by comparing the rates of hydroxide ion production at the surface exposed to sea water. Experience has shown that if a typical impressed current cathodic protection current density of 10 mA/ft2 is applied to steel in sea water, a measurable calcareous deposit will be formed over a period of months. This current density produces hydroxide ions at the rate of  $6.86 \times 10^{13}$  ions/cm sec. The production rate of hydroxide ion due to ammonia permeation at 77 F for a plastic heat exchanger with a wall thickness of 0.010 inch and a vapor pressure differential of 153 psi is 1.46 x  $10^{15}$  ions/cm<sup>2</sup> sec. This assumes that all ammonia arriving on the water side reacts to form hydroxide. Since this hydroxide ion production rate is some 21 times higher than that for cathodic protection, it is quite likely that formation of a calcareous deposit would occur, given the permeation rate of ammonia through unmodified HDPE.

#### SECTION 8

#### ANTIFOULING STUDIES

#### 8.1 GENERAL

Considerable effort has been spent in the development of various means to control biofouling of heat exchangers placed in seawater environments. However, due to the relatively small temperature differences across OTEC heat exchangers, it becomes paramount that minimal thermal resistances of the heat exchanger surfaces be maintained if the economical feasibility of the OTEC program is to be realized. It has been reported  $^{31}$   $^{32}$  that for titanium and aluminum heat exchangers in an OTEC applicator, a primary fouling film of .001 in. (.0025 cm) would result in a 10% decrease in the heat transfer coefficient whereas a .010 in. (.0254 cm) primary fouling film formation could reduce the heat transfer coefficient by as much as 50%.

It is not, however, the intent of this study to document the current state-of-the-art of methods for the control of biofouling on conventional heat transfer surfaces but rather to focus on methods for the control of biofouling on plastic heat exchangers which appear to offer several unique possibilities not inherent with metallic heat exchangers.

In order to assess the possibilities of developing methods for the control of biofouling it is first necessary to understand the mechanism by which fouling occurs. This subject has been previously reviewed by Haderlie and others 33, therefore only a brief review of these mechanisms will be presented below.

# 8.2 MECHANISMS OF BIOFOULING .

Biofouling of heat exchanger surfaces may be classified as either macro-fouling (i.e. barnicles, hydroids, algae, etc.) or microfouling (i.e. organic films, bacteria, diatom, etc.). Macrofouling is considered as the first type of fouling to occur and some studies have suggested that this type of fouling is a necessary prerequisite for macrofouling. In light of this and the magnitude of reduced heat transfer efficiencies which can be realized from this type of fouling, the emphasis of this discussion will be concerned with the mechanism of microfouling and its prevention and/or control.

The first film to form on the surfaces of a clean solid placed in natural seawater consists of dissolved or suspended organic matter which adheres to the solid substrate. It has been determined that this film consists of a monolayer of glycoprotein. This layer may then modify the "critical surface tension" thereby allowing bonding between the solid surfaces and the organic film containing the micropolysaccharide components of the first arriving bacterial cells. Baier to considers that these gycoprotein "conditioning films" are an essential prerequisite to later adsorption of any cellular material to solid substrates. However, Haderlie does stress the fact that although considerable data exists on the ecological succession of fouling communities, starting with the film forming bacteria, and that the formation of one group of organisms does effect the nature of subsequent colonizing organisms, experimental proof does not yet exist to substantiate the claim that prevention of the formation of this primary film will totally negate the formation of a fouling film.

Once the organic film is present, living bacterial cells are attracted to the film and subsequently adhere and colonize the surface. It has been known that the investigations into the chemotaxic responses of motile bacteria has revealed that these bacteria do tend to concentrate on surfaces possessing a primary organic film, thus implying that these bacteria are capable of detecting the films nutrients at a distance and move toward them.

Studies have shown that the behavior of motile bacteria as they approached and adhered to a solid substance and found two distance phases involved. The first phase of attachment may be described as a 'reversible sorption phase' where the electrostatic and hydrophobic forces of attraction are balanced against a double layer repulsion force. The net negative charge of the bacterial cell surface is repelled by the negative charge of the organic film indicating that the bacteria are capable of overcoming the mutually repulsive forces by following the concentration gradient of the nutrients of the molecular organic film. During this phase no direct contact with the surface is made and the bacterial cells may be removed by washing.

After reaching the surface of the organic film, the bacterial cells secrete an extracellular briding polymer which cements the cell to the surface. It refers to this attachment as the irreversible phase. In addition to bridging the cell surface of the bacterium to the substrate, this polymer also tends to collect various kinds of debris and rapidly creates a physically and chemically complex surface.

This secreted extracellular polymer may cover the substrate surface some distance from the producing cell and this polymer tends to adhere more tenaciously to the substrate than to the bacterial cell. In addition, the film forming cells and its associated secretions appear to be able to retain their enzymatic activity long after the death of the cell. Consequently, the remaining debris and polymer lay may continue to serve as a center of biochemical activity and influence the subsequent attraction and attachment of additional bacteria and debris.

The ecological succession of the biofouling of solid substrates immersed in a seawater may therefore be summarized accordingly:

- 1) Absorption of dissolved organics
- 2) Detection of a nutrient gradient by motile marine bacteria
- 3) Migration of bacterium to surface of the organic film
- 4) Irreversible attachment of bacteria cells
- 5) Accelerated absorption of additional debris, bacterium and
- 6) Colonization by hydroids, algae, barnacles (i.e., macrofouling).

#### 8.3 PREVENTION METHODS

#### 8.3.1 General

The current state-of-the-art for controlling gross biofouling has consisted primarily of either chemical disinfection or the use of toxic coatings.

# 8.3.2 <u>Chemical Disinfection</u>

The use of chemical disinfection is commonly practiced and utilizes such chemicals as chlorine, ozone, sodium sibulphite, etc. These agents operate by killing bacteria and the larva stages of macrofoulers before they have a chance to settle and colonize. The effectiveness of the chemical agents upon the bacterial primary films is not certain and the large quantities of chemicals which would be required for an OTEC application make this method unlikely. Some of these chemicals may retain their biocidal activity for some time consequently providing significant adverse ecological impacts which could negate the potential beneficial environmental impacts which could arise from the aquaculture of the nutrient rich waters discharged by the OTEC condensers.

# 8.3.3 <u>Toxic Coatings</u>

Another commonly utilized method for the control of gross biofouling utilizes the toxic effects of the salts of heavy metals and organometals. These coatings owe their effectiveness to a slow leaching into the surrounding water and the subsequent formation of an ionic halo over the surface which repells or kills the lava or spores of fouling organisms. Although effective in the control of macrofouling, considerable doubt exists as to the effectiveness of heavy metals, salts and organometalic in controlling the formation of "primary films".

Several reports<sup>35</sup>,<sup>36</sup>, have shown that these bacterial films are little effected by coatings, incorporated heavy metals or organotins. Corpe <sup>37</sup> reported that the film forming bacteria and their secreted acid polymeric cementing material were capable of binding and precipitating copper salts while other investigators have reported similar effects on cobalt, nickel, lead and zinc. This evidence suggests that primary film forming bacterial may settle upon the surface of antifouling coatings and accelerate the leaching rate of the metals thereby reducing the effective service life of the coating.

In the light of these findings, and the extensive research presently being undertaken in the development of organometallics heavy metal salts as methods for the control and prevention of biofouling, these methods were not considered as novel candidate methods for the prevention and control of "primary film" biofouling of plastic heat exchangers.

#### 8.3.4 UV Irradiation

The only method thus far successfully employed for the control of marine bacterial films is the irradiation of the surface with ultraviolet<sup>35,38</sup>. light. Although this method was successful in preventing the formation of bacterial films on the surface of periscope windows, it is not known whether the ultraviolet radiation prevents the film from forming by repelling or killing the bacteria before they settle, or if the radiation destroys or prevents the formation of the molecular organic film that occurs prior to bacterial attachment. However, it is unlikely that this method could be utilized in OTEC application due to the relatively shallow penetration of the effective UV radiation and the large quantities of water requiring treatment.

# 8.3.5 Low Energy Surfaces

It has been suggested that microbiological films might be controlled by manipulation of the "critical surface tensions" of the substrate surface. Bailer<sup>39,40</sup> has proposed a theory for explaining biofouling behavior of substrates in terms of surface energy effects. He proposes that the rate of fouling occurring on a submerged substrate is a function of its initial surface energy measured as an empirical parameter. He calls this parameter the "critical surface tension of wetting" (YC) and expects the rate of biofouling to be minimal between a YC range of 25-30 dyes/cm. Within this "biocompatible region", the chemical constituents of the slime layer absorb reversibly in an undenatured configuration while outside this region the glycoproteins become denatured and absorb irreversibly onto the surface.

Baire's hypothesis has been substantiated by Dexter<sup>41</sup> who reports that the rate of accumulation of bacteria on solid substrates differed with chemically different classes of materials when exposed to a marine environment for prolonged periods of time and that minimal accumulation of bacterial films occurred on substrates with initial surface energies in the 25-30 dynes/cm range.

# 8.3.6 Negative Chemotaxis

One of the most promising novel methods for controlling microfouling of plastic heat exchangers is based upon the microbiological process of negative chemotaxis. Mitchell $^{42}$  tested a wide range of organic compounds for their ability to repel motile isolates of marine bacteria and found the most effective repellents to be acrylamide, N,N,N'N' - Tetramethylethylene, diamine, indole, tannic acid, benzoic acid and phenylthiourea. These screening tests were conducted by placing a micropipette containing either nutrient broth (to test positive chemotaxis) and a candidate repellent (to test negative chemotaxis) and artificial seawater (as a control) into a bacterial suspension of marine motile bacteria. Repulsion, or negative chemotaxis, was estimated by determining the number of bacteria entering these micropipettes.

In order to test the relationship between negative chemotaxis and the possible prevention and/or control of primary film fouling, several plates were painted with a non-toxic neutral oil paint with some containing the organic compounds previously shown to possess negative chemotaxic characteristics. Test panels were then exposed to seawater off the coast of Ft. Lauderdale and the amount of slime was estimated both gravemetrically and by chemical analysis.

The control panels, painted but without the organic repellents, showed signs of slime accumulation in less than I weeks exposure reaching a maximum in a little over two weeks. The organic compound showing the greatest negative chemotaxic response was benzoic acid. When compared to the control panels, the panels painted with the oil paint and benzoic acid (less than 0.5%) showed a 95% reduction in the amount of slime formed on the panels. Almost as effective was tannic acid which showed a 94% reduction in slime formation. Moderately effective was Acrylamide exhibiting an 82% reduction while N,N,N'N' - Tetramethylethylenediamine and Phenylthiorea exhibiting 53% and 30% reductions.

Further testing of these organic compounds showed that the threshold concentration of these compounds was between  $10^{-7}$  and  $10^{-6}$  molar with optimal concentrations for repulsion being between  $10^{-3}$  and  $10^{-4}$  molar.

A major advantage to the use of these organic compounds to control microfouling lies in the fact that these compounds are effective as repellents at non-toxic concentrations. Tests conducted by Mitchell  $^{\rm 42}$  confirmed that neither the motility or viability of the bacteria were effected when placed in media containing the repellents at the concentrations tested (less than 10  $^{\rm 2}$ M). This characteristic will greatly minimize the potential for adverse environmental impact associated with the discharge of effluents of the condensers and evaporators of OTEC plants utilizing toxid compounds to control the various forms of biofouling and may greatly facilitate the use of the nutrient rich discharge of the OTEC condensers for aquaculture purposes.

# 8.4 METHODS OF REPELLENTS

# 8.4.1 General

Plastic heat exchangers are selectively permeable to a variety or organic and inorganic compounds. This property offers several advantages over conventional metallic heat exchangers in that the application of biofouling compounds is not restricted to coatings of the surfaces but may utilize the selective permeation characteristics of the plastic to control the release of the repellent into the seawater side of the heat exchangers directly at the interface where fouling occurs. In attempting to capitalize on this characteristic of the PLHX we have found three distinct routes which may be taken to bring the repellent to the seawater surface of the PHX.

# 8.4.2 Incorporating Method

The mostodirect means of utilizing these candidate repellents in PLHX applications would be to compound the repellent directly into the resin backbone prior to extrusion. This may be accomplished in much the same manner as is currently being utilized by Montemarano et al<sup>43</sup> to incorporate organometallics such as Tributyltin oxide and tripropytin oxide onto an acrylic backbone. This would involve a careful evaluation of the potential methods which would be required to compound these new polymers and a determination of any changes in the physical properties of the new repellent polymer. In addition,, an analysis would be necessary to determine the dissolution rate of the repellent into the seawater in order to project the proper repellent loading rate necessary to achieve a satisfactory effective life of the PLHX. Our preliminary investigations indicate that a trade off will exist between high repellent loading rates and the physical properties of the compounded polymer. It will also be necessary to determine the leach rate of the repellent into the working fluid and determine the effect, if any, upon the efficiency of the power cycle.

As an alternate to incorporating the repellent into the resin backbone it may be quite possible to absorb the repellent directly into the acetylene black prior to compounding the resin since, in order to increase the thermal conductivity of the polymer, loading rates of from 5 to 25% by wt. acetylene black were projected.

#### 8.4.3 Permeation Method

Again capitalizing on the semi-permeable nature of PHX another route for bringing the repellent to the seawater surface of the PHX is possible. This method would involve the incorporation of the repellent in the working fluid with subsequent permeation through the PHX providing the necessary concentration of the repellent on the seawater side of the heat exchanger to inhibit primary film formation. The viability of this process will depend largely upon the nature of the specific repellent utilized. Upon the selection of a particular repellent it will be necessary to determine the rate of permeation through the PHX as well as the concentration of repellent required in the working fluid to ensure an effective repellent concentration on the sea water side of the PHX. An evaluation of the effect of this concentration of repellent upon the efficiency of the power cycle will also be necessary.

In addition it will also be necessary to determine the rate of decomposition of the repellent in the working fluid environment as well as the chemical compatibility of the working fluid-repellent combination upon the PHX resin.

A major potential advantage of this method of utilizing repellents for controlling micro fouling stems from the fact that the repellent may be added to the working fluid on a continuing basis thereby not limiting the effective fouling free life of the PHX by the net quantity of repellent incorporated into the PHX resin.

# 8.4.4 Repellent Absorption

A third possible method involves the selective absorption of a repellent into the PHX with a subsequent slow release into the seawater. This would involve the isolation of one or both sides of a portion of the PHX and recirculating a strong concentration of a repellent solution until the PHX becomes essentially saturated with respect to the repellent. The system would then be brought back on line allowing the repellent to slowly leak out into the sea water. The optimum characteristic of the PHX which would favor this particular system would involve a PHX whose permeability to the repellent would be minimized on the seawater side. This could be accomplished by modifying the surface properties of the seawater side of the PHX either by surface treatments (such as sulphurtroxide) or by coextruding a barrier film on the sea water side of the PHX. These treatments would most likely necessitate the isolation of the working fluid side of the PHX only.

#### 8.5 CANDIDATE REPELLENTS

#### 8.5.1 General

The studies conducted by Mitchell<sup>42</sup>, <sup>43</sup> identified seven organic compounds which initiated negative chemotaxic responses of marine motile bacteria. Three of these offered significant reductions in slime formation when compounded into a neutral oil base paint. These were, in order of decreasing effectiveness, benzoic acid, tannic acid, and acrylamide.

# 8.5.2 Benzoic Acid (C<sub>6</sub>H<sub>5</sub>COOH)

Our preliminary investigation of these candidate organic repellents indicates that baenzoic acid offers the greatest potential for utilization in an OTEC application. In tests conducted by Mitchell $^{42}$ , benzoic acid showed the greatest reduction in slime formation on test panels. The cost of industrial quantities of benzoic acid is approximately 0.36/%, lowest of the three most effective organic repellents tested.

It is one of the simplest aromatic acids with an MW of 122.05 thereby suggesting a significant potential for permeation thru PHX.

Upon contact with ammonia the following reaction may occur.

$$\bigcirc$$
 COOH + NH<sub>3</sub>  $\bigcirc$  COONH + H<sub>2</sub>O  $\bigcirc$  COO + NH<sub>4</sub>  $\bigcirc$  Benzoic Acid Ammonium Benzoate

Upon contact with seawater two possible reactions, both resulting in the formation of sodium benzoate.

Mitchell<sup>42</sup> reports however, that satisfactory negative chemotaxid responses were noted when benzoic acid was added to a saline media as well as when the benzoic acid was incorporated into the neutral oil base paint and subsequently immersed in seawater. In both instances the end product is a carborylic acid salt thereby suggesting that it is either this salt or the disassociated  $\bigcirc$  COO ion which initiates the negative chemotaxic response in marine micro-organisms.

# 8.5.3 Tannic Acid

Tannic acid was the second most effective organic repellent identified, offering about the same efficiency in preventing slime formation of test panels. However, the high cost of industrial quantities of tannic acid, approximately \$3.42/#, make the economical use of this compound in an OTEC application unlikely. In addition, the molecular weight of tannic acid is about 1700, suggesting that the permeation of this compound through the PHX may not be sufficient to maintain a satisfactory concentration of tannic acid on the seawater side of the PHX to initiate a negative chemotaxic response of marine micro-organisms coming in close proximity to the PHX surface.

# 8.5.4 Acrylamide $(CH_2CHCONH_2)$

Acrylamide was the third most effective organic repellent identified and although the cost of industrial quantities is moderate, about \$0.46/#, several other properties of this compound may prevent its use in an OTEC application. The most significant being the toxic nature of the compound to humans. It is toxic by ingestion, inhalation of vapor, dust, or aerosols and by skin absorption. It attacks the central nervous system and causes acute and severe chronic intoxication, thereby requiring extensive safety measures to insure adequate employee protection.

It also tends to polymerize rapidly when exposed to high temperature, UV radiation and a wide range of catalyst thereby necessitating special storage and handling facilities. The polymerization reaction is very exothermic providing additional fire hazards.

Once polymerized the MW of the polymer may easily reach 1 million greatly reducing the permeation and subsequent dissolution into the sea waterheat exchanger interface.

#### 8.6 RECOMMENDATIONS

The potential of utilizing the negative chemotaxic responses of marine vacteria to organic repellents incorporated in plastic heat exchanger materials appears to be a viable means of controlling and/or preventing the biofouling of these surfaces but several areas of uncertainty must be further defined and demonstrated before an accurate assessment of this potential may be made. Following is a brief description of some of these areas which, when further defined, may assist in this evaluation.

- 1) An evaluation of the alternatives and demonstration of the feasibility of incorporating candidate organic repellents into plastic heat exchanger resins and the effect of these repellents upon the physical properties of the compounded resin.
- 2) A determination of the dissolution rate of the repellent from the resin into both sea water and candidate working fluids.
- 3) Determination of the effect, upon the efficiency of the power cycle, of varying concentrations of repellents in the working fluid.
- 4) A determination of the permeation rate of the repellent through the PHX material when the repellent is incorporated directly in the working fluid.
- 5) A determination of the rate of decomposition of the candidate repellents in contact with the working fluids.
- 6) A determination of the chemical compatibility of the working fluid repellent mixture upon the PHX resin.
- 7) Determination of the rate and maximum loading of the absorption of candidate repellents into the PHX resin.
- 8) Determination and demonstration of effective repellent concentrations required at the seawater heat exchanger interface to control or prevent biofouling under OTEC simulated conditions.
- 9) Identification of additional candidate organic repellents whose properties may be better suited to OTEC applications.

#### SECTION 9

#### CONDENSER TEST UNIT DESIGN

#### 9.1 INTRODUCTION

The primary unknown in plastic heat exchanger design, the performance of the materials themselves, has been addressed by this study. Perhaps the most significant question raised by the previous report¹ was whether a plastic could demonstrate the required durability in the OTEC environment. This has been answered affirmatively by the experimental results in this report.

It was recognized in 1977 that the plastic materials testing and evaluation program was sufficiently advanced to make a material selection and provide the basic engineering data needed for the design of a heat exchanger test unit. At that time, plans for an OTEC heat exchanger test facility at Argonne National Laboratory were also well underway. The scope of work for the current program was, therefore, modified to include the design of a condenser core test unit.

#### 9.2 MECHANICAL FABRICATION

Our feasibility study indicated that a shell-less plate type configuration has advantages that make it especially attractive for a PHX. The most notable of these advantages are: 1) design freedom for working fluid passage geometry; 2) independence of sea water passage dimensions from material property constraints; 3) ability to utilize large, extended panels and; 4) lack of a pressure vessel shell. Accordingly, a plate type ammonia condenser of 900,000 Btu/hr nominal duty was designed. A condenser was selected as the lower risk heat exchanger for a first effort because it lacked the potential fluid distribution and instability problems of evaporators.

#### Pressure Vessel

The core of PHX is housed in a pressure vessel for safety reasons and to avoid the necessity of providing a free surface on the water side. As shown in the assembly section, Figure 9-1, the unit will outwardly resemble a shell-and-tube heat exchanger. Table 9-1 is a summary of the preliminary condenser design of a single pass on the water side.

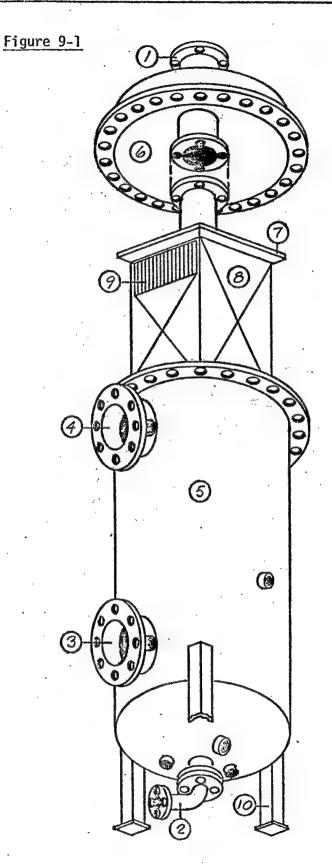
The outer shell will be a cylinder carbon steel pressure vessel designed to the ASME pressure vessel code, section VIII - for a working pressure of 215 psig the detailed design and deminsions of this pressure vessel is shown in Drawing No. 059-2201. The vessel nozzles are also identified in Table 9-2.

# Bundle Fabrication

The condenser core consists of extruded HDPE "plate-tube" panels. As produced, these panels are 10 ft long and 4 ft wide with the channel cross section geometry shown in Figure 6-5. The panels were extruded

# PHX TEST UNIT ASSEMBLY SKETCH

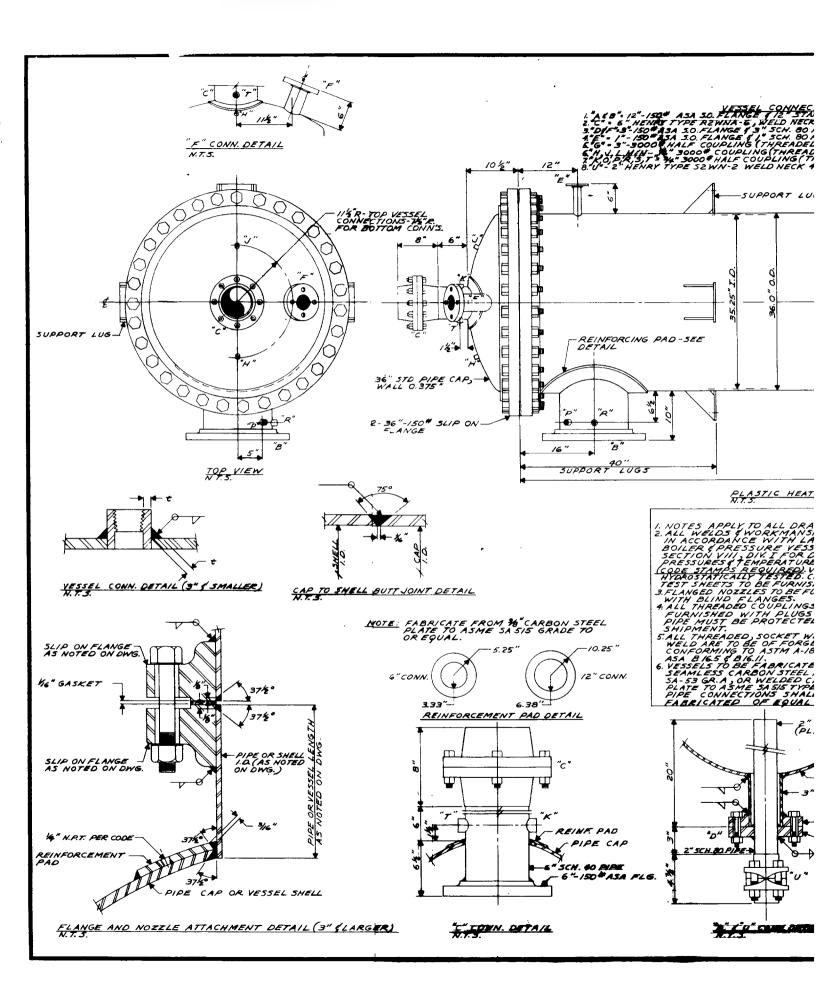
- 1. AMMONIA VAPOR INLET
- 2. AMMONIA CONDENSATE OUTLET
- 3. WATER INLET
- 4. WATER OUTLET
- 5. OUTER SHELL
- 6. OUTER HEAD
- 7. UPPER CORE HEADER
- 8. CORE SHROUD
- 9. PLASTIC CORE
- 10. SUPPORT LEG



P.S. 10/77

# Table 9-1 Condenser Design Summary

. ,	•	·
Shell Material		Carbon Steel, SA515 type 70
Panel Material	. =	Type III Polyethylene
Shell-side Fluid		Water
Panel-side Fluid	_	Ammonia
Shell Design Pressure	-	215 psig
Panel size (width x length)	•	17" x 120"
Panel wall thickness	-	0.026"
Number of Panels	-	34
Outside Heat Transfer Area (based on nominal panel width)		842 ft <sup>2</sup>
Panel Spacing (center-to-center)		0.52"
Shell Diameter	**	36"
Height Overall	<b>~</b>	12' 3"
Approximate Empty Weight	. 🐃	3600 1bs
Approximate Water Weight	-	7700 1bs
Approximate Ammonia Weight	-	40 1bs
Ammonia Condensate Level (from C.L. of condensate nozzle)	-	•
Overhead Required for Core Removal	_	25'



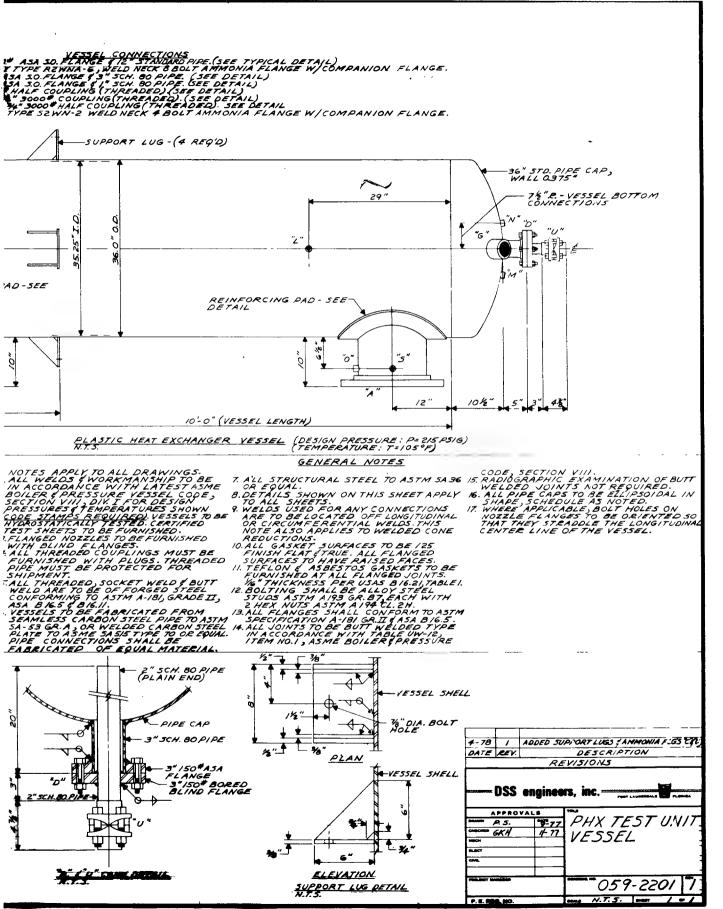


Table 9-2
PHX Test Unit

# Outer Vessel Nozzle Identification

NOZZLE	SIZE	TYPE	FUNCTION
<b>A</b> .	14	150# flgd.	water inlet
В	14	150# flgd.	water outlet
. <b>C</b>	8	300# flgd.	ammonia vapor inlet
D	2	300# flgd.	ammonia condensate outlet
E	1	150# flgd.	shell side safety valve
<b>F</b>	. 3	150# flgd.	instrumentation
G	3	3000# scd.	access "
H	1/4	ts.	vent
I			
J	1/4	ti .	instrumentation
K	3/4	ft.	
L	1/4	. 19	n
M	1/4	· a	n n
N	3/4	b	drain
0	3/4	<b>29</b> .	instrumentation
P	3/4	n ·	H
Q			
R	3/4	er e	H
S	3/4		a a
<b>T</b> .	3/4	. 81	- <b>1</b> 11

in Soltex F364 HDPE using existing tooling that is normally used for a polypropylene copolymer. Hydrostatic tests have indicated a short term internal burst pressure of 750 psi and an external collapse pressure of 220 psi for this panel.

It was recognized during the design of the test unit that only thermal welding could provide the reliable leak-proof joints required for assembly of the HDPE core panels. Fortunately, welding can be accomplished by a number of techniques differing mainly in the manner of producing heat at the joint. The critical joints in this case are the ones between the panels or panels and spacers at the core headers; they must be leak-proof and preferably provide a bond equal in strength to the panels themselves. Some of the techniques actually tried are:

- 1. three types of hot tool welding
- 2. hot gas welding with filler rod
- 3. hot gas tacking tip (a combination of hot gas and hot tool welding)
- 4. hot gas "tube" expander nozzle (another hot gas-hot tool combination)
- electromagnetic induction welding

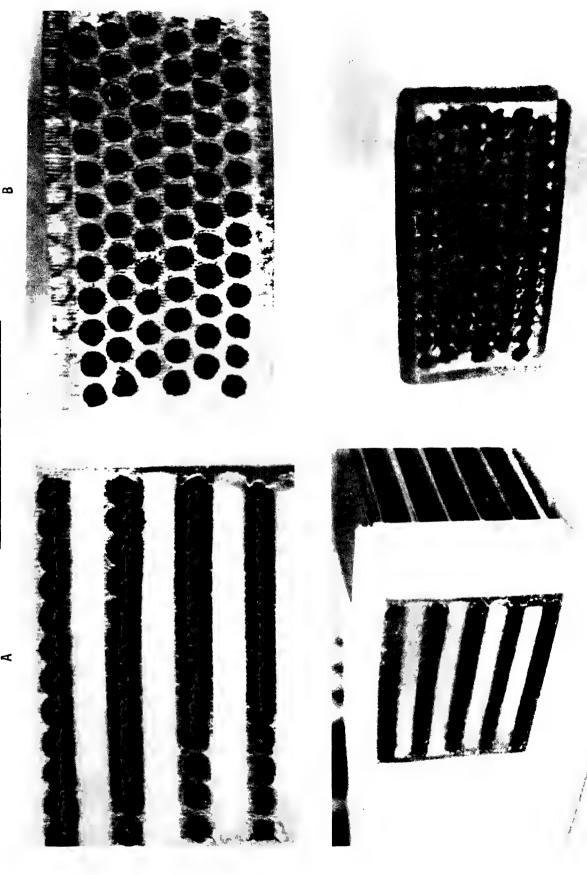
All of these techniques were successful in varying degrees depending on process variables and operator skill. Hot tool welding was used to produce 60 test specimens of the type shown in Figure 7-1 with a zero scrap rate. For assembly of large bundles, however, electromagnetic induction welding appears to be the superior technique.

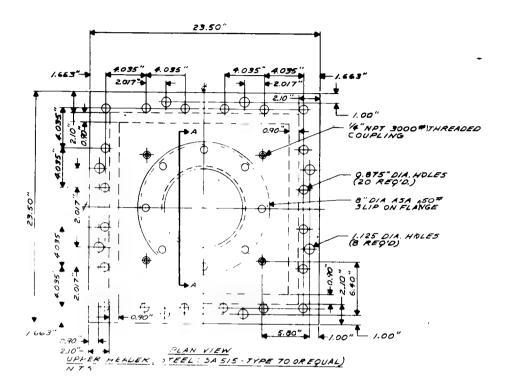
The principle of the induction welding is based on the fact that magnetic materials develop heat loss when exposed to a magnetic field. This magnetic field is generated by a high-frequency induction source. Micron-sized magnetic particles are dispersed within a thermoplastic matrix. In our cases, the magnetic material is stainless steel 400 powder and the thermoplastic is high density polyethylene. When this filled material is placed between the surfaces to be welded and exposed to a magnetic field, heat develops at the interface causing melting and subsequent fusion of thermoplastic materials. This welding method can produce joints of large area even with thin wall profiles, does not depend on operator skill and is easily adapted to automated assembly. We have, therefore, selected this method for core test unit fabrication.

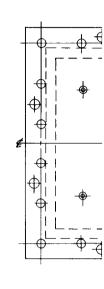
Two configurations of the core at the headers have been tried. If spacers are used between the individual panels a rectangular core will result, but if the panels are bonded directly to each other, the bundle will assume a "bottleneck" shape at top and bottom. Figure 9-2 shows details of these two configurations executed with induction welding. Also, in this figure the spacers and panels are of contrasting color. The bottleneck configuration has the following advantages: 1) it eliminates most of the "tubesheet" area; 2) it requires about one half the number of welded joints and; 3) for the test unit, it allows slightly more heat transfer area to be installed in a given size shell. The detailed bundle design is shown in Drawing Nos. 059-6901, 059-6902, 059-6903 and 059-6904.

#### 9.3 THERMAL PERFORMANCE

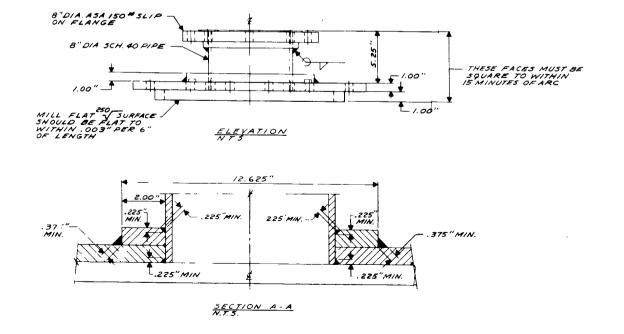
The calculated thermal performance for a single pass unit is shown in Figure 9-3 and nominal thermal and hydraulic figures presented in Table 9-3.





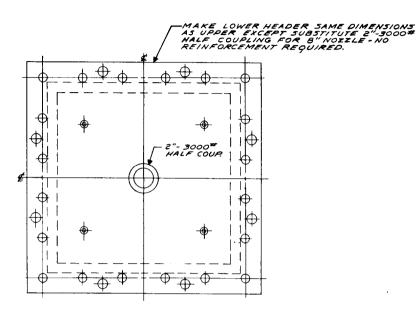


LOWER HEADER ( 5TE

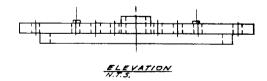


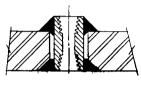


1. GENERAL NO. NOTED. 2.NO CODE 5: 3. UPPER AND TESTED AS 4.BLIND FLAI COUPLINGS 5. GASKETS NO.



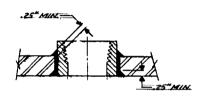
PLAN VIEW LOWER HEADER (STEEL: SASIS-TYPE TO OR EQUAL)



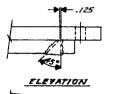


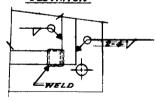
. . . .

1/4" FULL COUPLING



Z" HALF COUPLING





PLAN

CORNER VOINT DETAIL

GENERAL NOTES

1. GENERAL NOTES OF DWG NO. 059-2207 APPLY EXCEPT AS OTHERWISE NOTED.

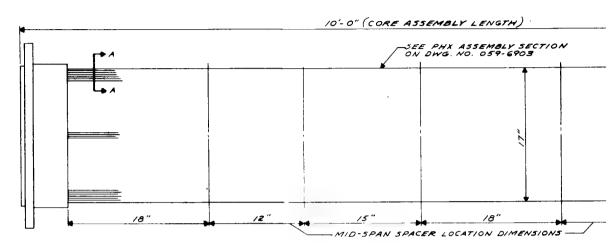
2. NO CODE STAMP REQUIRED.

3. UPPER AND LOWER HEADERS TO BE MATED AND HYDROSTATICALLY TESTED AS A PAIR. NO TEST CERTIFICATION REQUIRED.

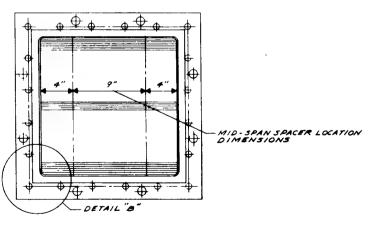
4. BLIND FLANGE FOR UPPER HEADER AND PLUGS FOR THREADED COUPLINGS NOT REQUIRED.

5. GASKETS NOT REQUIRED.

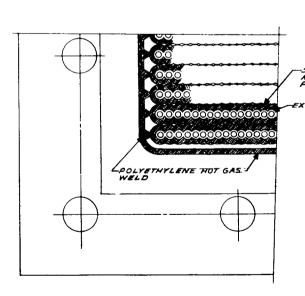
DSS engine	Bers, inc.
APPROVALS  DRAWN P. S. 73/7  CMECKED G. M. M. /2/7  MICH  BLACT  CAYL	
PROJECT MANAGER	059-6901
P. E. REG. NO.	SCALE N.T.S. SHEET / OF /



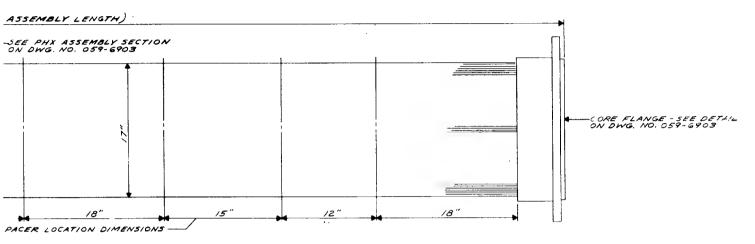
SIDE ELEVATION-CORE ASSEMBLY
SCALE: 1:5



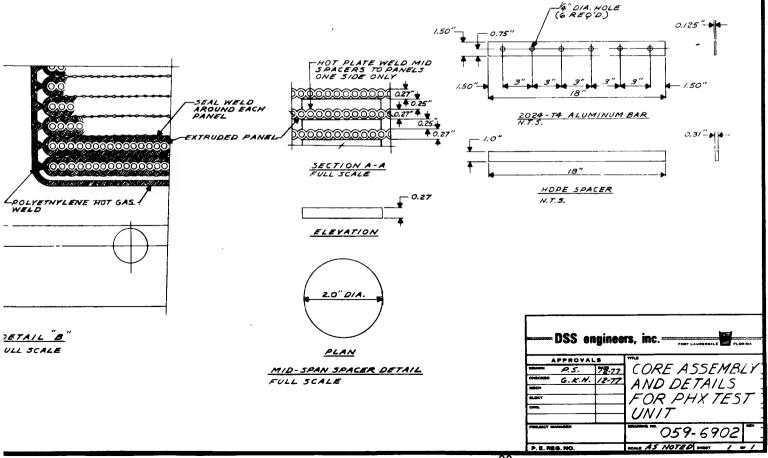
FRONT ELEVATION - CORE ASSEMBLY SCALE: 1:5

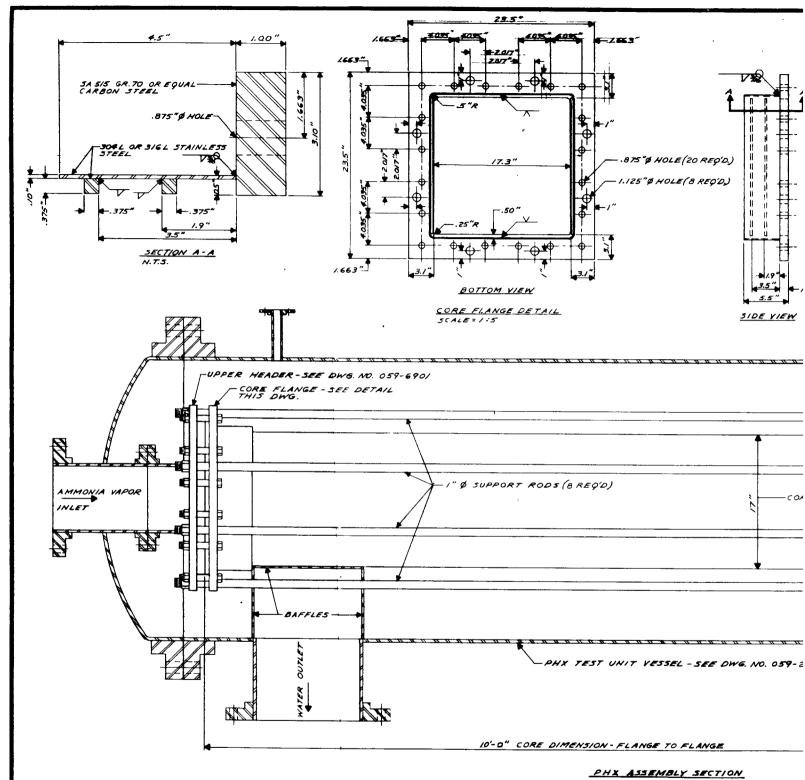


<u>DETAIL "B"</u> FULL SCALE

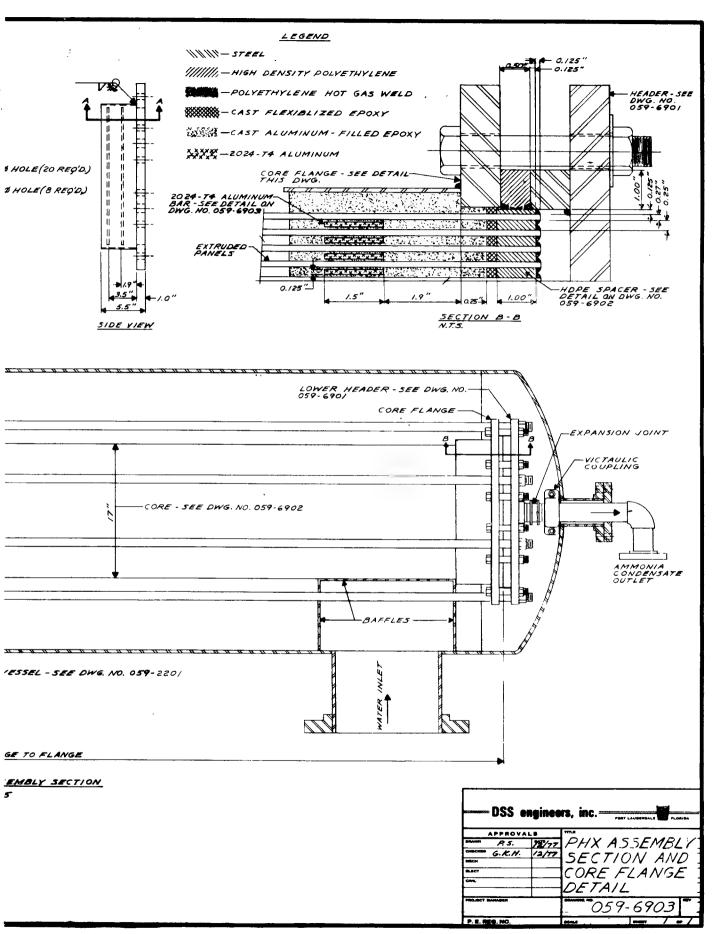


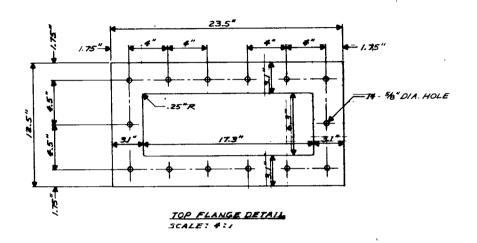
FVATION - CORE ASSEMBLY
1:5

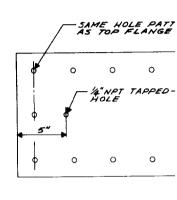




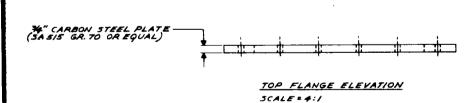
SCALE: 1:5

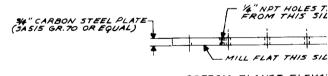






BOTTOM FLANGE D 5CALE = 4:1





BOTTOM FLANGE ELEVA: 5CALE = 4:/

LEGEND

|||||||- STEEL

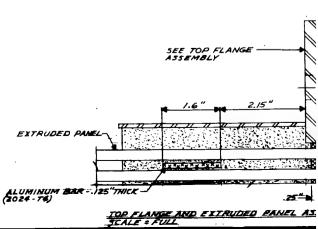
///////,- HIGH DENSITY POLYETHYLENE

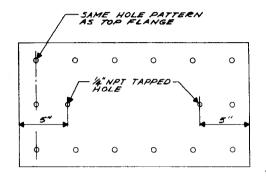
- POLYETHYLENE HOT GAS WELD

CAST FLEXIBLIZED EPOXY

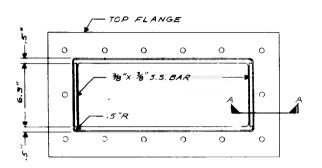
(AST ALUMINUM - FILLED EPOXY

XXXX - 2024 - 74 ALUMINUM

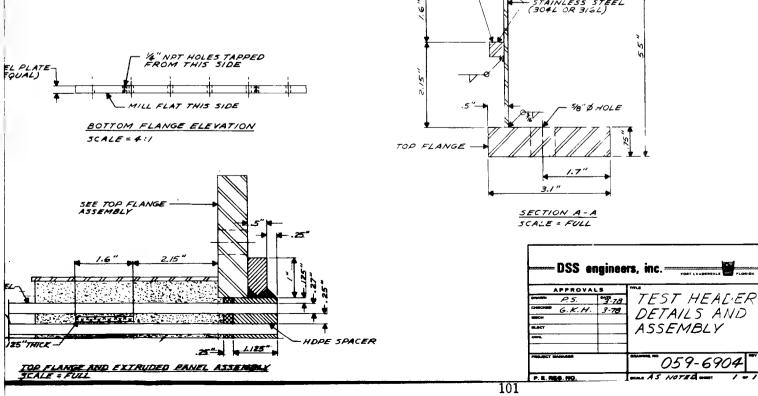




BOTTOM FLANGE DETAIL
SCALE : 4:1



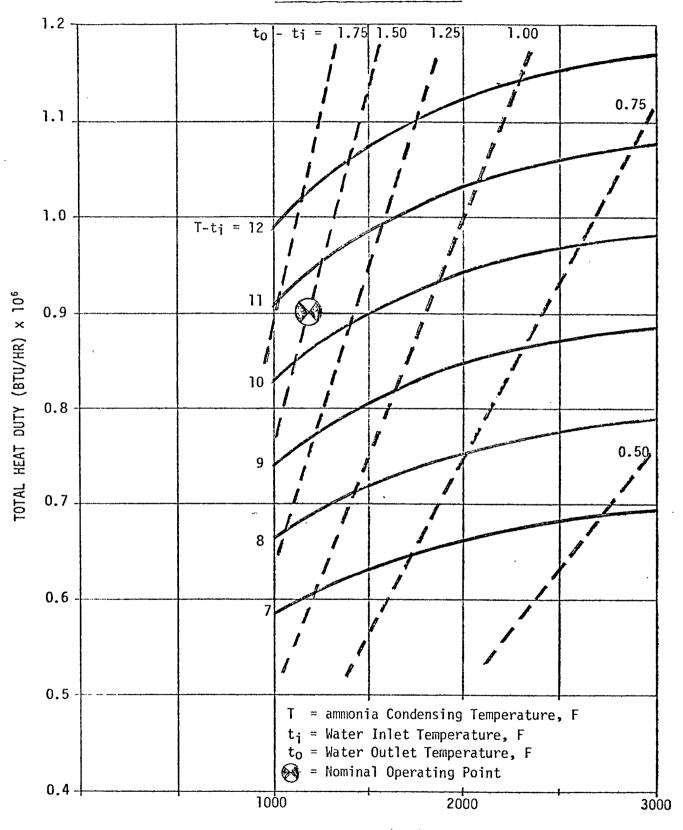
TOP FLANGE ASSEMBLY



38"X 36" 5.5. BAR

<u>Figure 9-3</u>

<u>Thermal Performance of Condenser Core Test Unit</u>



WATER FLOW (GPM)

Table 9-3
Condenser Nominal Operating Conditions

Saturated Vapor Quality, %	100
Heat Duty, 10 <sup>6</sup> Btu/hr	0.90
Ammonia Inlet Temperature F	50.0
Cold Water Inlet Temperature, F	39.5
Water Temperature Change, F	1.5
Log Mean Temperature Difference, F	<b>9.7</b> :
Condensate Sub-cooling, F	0
Water Flow Rate, gpm	1200
Water-side Pressure Drop, psi	0.25
Water velocity, ft/sec	2.25
Ammonia-side Pressure Drop, psi	<0.02
Ammonia Mass Flux, lb/ft² sec	0.91
Ammonia Condensate Flow, gpm	5.5

The primary objective of this test unit is to establish a "baseline" overall heat transfer coefficient for a PHX with very conservative mechanical design. Because an unfilled HDPE with a thermal conductivity of 0.25 Btu/hr ft² F has been used for the panels and because the profile has heavier-than-necessary walls, thermal performance of an actual OTEC condenser would be considerably better than that attained by the core test unit. Another difference between the test unit and a large condenser is the use of counter-flow rather than a cross-flow configuration; this is necessary to provide a water flow path of sufficient length to obtain a reasonable temperature rise.

The ammonia side film coefficient has been calculated from the classical Nusselt relation for filmwise condensation. Although there would be a strong initial tendency for dropwise condensation of fluids with high surface tension on a polyethylene surface, critical surface tension data for polyethylene indicates that it wouldbe wet by ammonia. The low ammonia mass flux for the test unit results in a laminar condensate film and negligible vapor shear. Ammonia side pressure drop should be less than the instrument's minimum measurement capability.

Wall thermal resistance for the test unit is about 75% of the overall resistance. This fact and the straightforward nature of the condensation process should make it possible to calculate the overall heat transfer coefficient with zero water side resistance. By varying water velocity, the dependence of the water side film coefficient on velocity can be established for the unusual water channel configuration. For the performance calculations, it has been assumed that Nusselt number varies as the Reynolds number to the 0.8 power.

# APPENDIX A

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#### APPENDIX B

#### POLYETHYLENE

Polyethylene is presently one of the two largest tonnage plastics. It is sometimes also referred to as polythene although polyethylene is chemically the more correct term. It is defined by its name as a homopolymer of ethylene produced by additional polymerization and as such may be described as a linear polymer with the formula  $(CH_2)_N$ 

Polyethylene is now produced by several processes, each resulting in resins possessing differing characteristics. Generally, each resin may be classified into three main categories based on their density. These classifications are identified in the following table.

<u>Density</u>	Rang	<u>e</u>	Type	Common Designation
Low Medium	0.910 0.925	0.925 0.940	I II	"Branched", LDPE MDPE
High	0.940	0.965	III	"Linear", HDPE

#### Structure

Polyethylene is essentially a non polar, long chain, aliphatic hydrocarbon. It is partially amorphous and partially crystalline with the degree of side branching being a key factor controlling the degree of crystallinity.

The type of processing can have several effects on the ultimate structure of the polymer and consequently alter the physical properties of the polymer.

Generally, high density polyethylene has fewer side-chain branches than low density polyethylene and consequently a more tightly packed structure and a higher degree of crystallinity can be obtained. Crystallinities of about 90% are common for high density polyethylenes whereas crystallinities of about 50% are obtainable for low density polyethylenes.

In general, polyethylene resins have good electrical properties, good chemical resistance, toughness, flexibility even at low temperatures, good water vapor barrier properties, and high resistance to water absorption. Under load polyethylene will deform continuously with time (creep). In general there will be an increase in creep with increased load, increased temperature, and decreasing density. Mechanical properties are very dependent on molecular weight and on the degree of branching in the polymer. Consequently, elongation at break is strongly dependent on density, the more highly crystalline high density materials being less ductile although even HDPE may draw rather than rupturing during tensile testing (depending on testing speed).

#### Chemical Resistance

Polyethylene in essence is a high molecular weight paraffin and as such can be expected to have good chemical resistance. Because it is a crystalline material and does not enter into specific interactions with any liquids, (e.g.hydrogen bonding) there are no solvents at room temperature.

Polyethylene is susceptible to stress-cracking in certain environments. The rapidity of failure is dependent upon the amount of stress and the temperature. Environments most conducive to stress cracking include surface-active wetting agents such as metallic soaps, sulfated and sulfonated alcohols. Environments such as aliphatic and aromatic hydrocarbons and specific organic acids introduce stress cracking to a somewhat less active degree. Which type of polyethylene is more resistant to environmental stress-cracking depends on the type of mechanical loading; low density types are generally more resistant where severe flexure is involved and high density types better for constant tensile loading.

# Application

HDPE has the highest thermal conductivity of all commercial thermoplastics, is very inexpensive, is expected to have good chemical resistance to OTEC working fluids and is easily processed. Disadvantages for OTEC application include relatively poor long-term strength, susceptibility to environmental stress-cracking and static fatigue and the inability to solvent bond.

Cross linked polyethylene tubes have been used in experimental heat exchangers for sea water desalination plants by at least three different investigators. For that application, cross linking was necessary for temperatures of 180 F and over.

# Polypropylene

Polypropylene is one of the large tonnage polyolefin thermoplastics rapidly becoming the most widely used thermoplastic material in industries involved with the manufacture of consumer products.

# Structure

Polypropylene consists of an ordered arrangement of repeating propylene monomer units. Its spatial regularity and close packing of adjacent chains yields a crystalline macrostructure. Usually about 90% of the polymer formed is isotactic (crystalline) and the remaining 10% is atactic (amorphous) which is usually stripped from the product at the conclusion of polymerization.

#### Properties

ing property. It possesses excellent physical properties which make it useful in load-bearing applications. These properties are dependent upon the amount of isotactic material present in the polymer. The greater the amount of isotactic material, the greater the crystallinity and hence the greater the stiffness, tensile strength, modulus, hardness, and chemical resistance.

# Chemical Resistance

The chemical resistance of polypropylene is generally very good, the major exception being susceptibility to oxidation. It is resistant to solutions of inorganic salts, mineral acid and bases. Most organic chemicals have no effect.

Polypropylene and High Density Polyethylene have many similarities in chemical resistance both having about the same solubility parameters, and tendency to be

swollen by the same liquids. As with polyethylene, the absence of any interaction between the crystalline polymer with liquids prevents solution of the polymer in any liquids at room temperatures.

It has been reported that polypropylene is free from environmental stress-cracking. However, data indicates that some environmental stress-cracking may occur.

In summary, the properties of polypropylene are very similar to those of high density polyethylene, with the following exceptions:

- 1) it has much lower thermal conductivity
- 2) it has a higher softening point and hence a higher maximum service temperature
- 3) it appears to be virtually free from environmental stresscracking problems
- 4) it is more susceptible to oxidation

# Application

Polypropylene's outstanding advantage over HDPE for core material application may be its freedom from environmental stress-cracking. It shares HDPE's other disadvantages and, in addition, has much lower thermal conductivity.

Biaxially oriented polypropylene tubes with 0.75" 0.D. and 3 mil wall are presently being used in an experimental heat exchanger for a desalination plant in Israel. The tubing itself, however, was developed in the U.S. This application takes advantage of polypropylene's high temperature capability and improved mechanical properties due to orientation.

#### Polybutylene Polybutylene

Polybutylene is the newest of polyolefin resins. It is a high molecular weight isotactic polymer synthesized from butene-1 monomer.

#### Structure

Polybutylene is a crystalline thermoplastic composed of linear chain molecules having a regular and spatially ordered arrangement of ethyl oxide groups along the chain backbone.

# <u>Properties</u>

The outstanding properties of polybutylene are its flexibility, creep resistance, (especially at high temperatures) and resistance to environmental stresscracking. As a result of its creep resistance polybutylene pipe has recieved a 2000 psi hydrostatic design basis stress at 73 F from the Plastics Pipe Institute. This is the highest pressure rating established for any of the polyolefins. It is reported that polybutylene accepts high filler loading (up to 85% by wt.)

# Chemical Resistance

Like the other polyolefins, the chemical resistance of polybutylene is generally good. It does, however, absorb some aliphatic hydrocarbons at room temperature but has no true solvents.

# Application

Polybutylene may best be compared to polypropylene. Its main advantages are higher thermal conductivity and better creep resistance. Disadvantages are higher cost and relatively small resin production at present. The only known heat transfer applications at the present time, solar collectors and snow melting coils, utilize the materials high temperature capability.

# **NYLONS**

Nylons, also called polyamides, are strong, tough thermoplastics having good impact, tensile, and flexural strengths as well as good chemical resistance and were the first family of materials now called engineering thermoplastics. The types of nylon which were considered are, Nylon 6, Nylon 6/6, Nylon 6/10, and Nylon 11.

# Structure

Nylons are linear, crystalline polymers having aliphatic chain segments containing amide groups at regular intervals. The number designation for each type of nylon indicates the size of the repeating units in the chain.

# Water Absorption

All nylons are hygroscopic and the amount of water abosrbed will effect both the dimensional stability and physical properties of the polymer. The greater the degree of crystallinity the less the water absorption and consequently the less will be the effect of humidity on the properties of the polymer. The effect of moisture absorption on the dimensional stability of a molded nylon specimen is to increase the specimen dimensions proportional to an increase in the amount of moisture absorbed. This effect is minimized by an opposing tendency of nylon parts to shrink in the direction of melt flow due to the relief of molded-in stresses.

The absorbed water has a plasticizing effect on the physical properties of the polymer, the result being that an increase in the amount of moisture abosrbed tends to decrease the ultimate tensile strength, tensile strength at yield, and the modulus while increasing elongation and compact strength.

#### Chemical Resistance

Because of the high cohesive energy density and their crystalline state, Nylon polymers are soluble only in a few liquids of similar high solubility parameters and which are capable of specific interaction with the polymers. Nylons have exceptionally good resistance to both aliphatic hydrocarbons and to hydrolysis. These properties make nylon particularly applicable in services where resistance to various chemicals is important. Notably services requiring exposure to gasoline, liquefied ammonia, alkalies, and organic acids.

# Type Selection

Since all four types of nylon evaluated have approximately the same mechanical properties it was necessary to select one type which appeared most promising for potential development as a core material for Plastic Heat Exchangers. Examination of available data indicated that Nylons 11 has the greatest application as a chemically resistant polymer and at the same time possesses a very low moisture absorption tendency thereby providing good dimensional stability. Water vapor transmission of Mylon 11 film is also lower than films produced from the other Nylons investigated. An added advantage of choosing Nylon 11 is that the manufacture of this resin has been successfully filling Nylon 11 with various metallic fillers (notably iron and aluminum) in concentrations as high as 75% by wt. At present there is no commercial market for these filled nylons and consequently a great deal of processing experience does not exist. The manufacturer, however, does feel confident that this material can be successfully extruded.

# Application

Nylon II balances its lower conductivity and higher resin cost relative to HDPE with higher long term strength, thus allowing thinner walls for a given geometry. A fabrication advantage it enjoys over the polyolefins is the ability to cement or solvent bond to itself and other materials.

#### **ACETALS**

Acetals, or Polyacetals as they are sometimes called are linear polymers with a flexible chain backbone and are thus thermoplastic. Due to their high cost and superior properties acetals, like nylons, are considered to be "engineering" rather than general purpose plastics.

#### Structure

The structure of Acetals closely resembles the structure of polyethylene, the difference being that acetal polymer molecules have shorter backbone bond and pack more closely together than those of polyethylene. The resultant polymer is harder and has a higher melting point. The acetal polymers are also highly crystalline.

# <u>Properties</u>

Acetal polymers possess high tensile strength, stiffness, resilience, and good recovery from deformation under load. They also exhibit excellent long-term load-carrying properties and dimensional stability. Although in many respects acetal resins are similar to the nylons, they may be considered to be superior to them in their fatigue endurance, creep resistance, stiffness and water absorption.

#### Chemical Resistance

Acetal polymers have excellent resistance to most organic solvents, including aliphatic hydrocarbons. Environmental stress-cracking has not been encountered in any organic solvents. Water does not cause any significant degrading hydrolysis of the polymer but may swell or permeate through it.

# Resin Selection

The first commercially available acetal resin was Delrin (duPont), a homopolymer produced by the polymerization of formaldehyde. The only other commercially available acetal resin is Celcon (Celanese), a copolymer of trioxane. The choice of the copolymer was based mainly on the reported better resistance to alkaline solutions.

# Application

Like nylon 11, acetal's suitability for OTEC application is based on its long term strength and chemical resistance. Besides its use as a core material it is also attractive for structural applications such as tubesheets and spacers because of its rigidity and the fact that strong solvent bonds to itself or nylon are possible.

# CELLULOSE ACETATE BUTYRATE (CAB)

CAB is one of the cellulose plastics, the oldest family of commercial thermoplastics. Unlike the other candidate core material plastics, CAB is produced by modifying cellulose, a natural polymer, rather than by polymerizing a monomer.

#### Properties

The chief characteristics of CAB is its toughness, dimensional stability and ease of processing. CAB is less hygroscopic than the other cellulose plastics and is less subject to plasticizer migration.

# Chemical Resistance

CAB is very resistant to most aqueous solutions of moderate pH and to aliphatic hydrocarbons. It has been reported that CAB showed no effects of one year's exposure to liquid propane.

#### Application

CAB was chosen specifically for compatibility with propane or isobutane working fluid. Resistance to ammonia is doubtful.

# POLYVINYLCHLORIDE (PVC)

Polyvinylchloride is the most commercially important and widely used of the vinyl polymers. It is available commercially as one of three types. Type I is a rigid, unplasticized, chemically resistant, normal impact grade. Type II is a slightly less chemically resistant plasticized grade. Type III is a high impact grade.

#### Structure

PVC is structurally based on an ethylene chain (as is polyethylene). However, the presence of the chlorine atom causes an increase in inter-chain attractions and hence an increase in the hardness and stiffness of the polymer. The presence of the carbon-chlorine dipole also makes the polymer polar and thus effects the chemical resistance.

In general, the performance characteristics of polyvinylchloride polymers include mechanical toughness, good weathering resistance, good chemical resistance and outstanding long term strength.

# Chemical Resistance

Polyvinylchloride possesses a very limited solubility and the only solvents that are effective are those which are capable of some form of specific interaction with the polymer. It has been suggested that polyvinylchloride is capable of acting as a weak proton donor and thus effective solvents could be expected to be weak proton acceptors. The result is that rigid polyvinylchloride (Type I) is completely resistant to inorganic alkalies in all concentrations. It is also resistant to all inorganic and organic salts and oxidizing agents as well as to hydrocarbons.

# <u>Application</u>

The outstanding qualification of Type I PVC is its long term strength; the hydrostatic design basis stress for PVC pipe compounds is as high as 4000 psi. Like acetal, PVC may also be useful for structural applications because of its rigidity and solvent bonding ability. Type I PVC is probably the most difficult of the candidate resins to extrude. Hydrocarbon working fluids would probably be compatible but resistance to ammonia is questionnable.

# APPENDIX C CHEMICAL RESISTANCE TEST DATA

Mechanical Properties after 7 day exposure at 80 F

		01		Tens	ile Stres	s, psi	Elonga-	*	Modulus
Test #	Medium	Orient- ation	Plastic	Max	Yield	Break	tion at Break %	M.R.S., psi/sec	x 10, <sup>5</sup> psi
1	AIR	. <b>Y</b>	CAB	4435	3468	4435	62	105	1.77
2		Y	CAB	4452	3468	4452	63	105	1.79
3		Υ.	CAB	4105	3387	4105	54	105	1.66
4	,	X ·	CAB	3991	3297	3991	55	102	1.75
5		х	CAB	4400	3347	4400	61	104	1.78
6		х	CAB	4220	3314	4220	58	104	1.74
7	ľ	Y	PB	2475	2020	2475	42	38	.546
8		Y	PB	2400	1965	2400	39	36	.484
9,		Y	PB	2327	1980	2327	28	36	.490
10		<b>X</b> .	PB	2376	1923	2376	31	. 35	.485
11		Х.	PB	2318	1995	2318	26 <sup>-</sup>	35	.453
12		х	PB	2333	1984	2333	25	35	.505
13		Y	HDPE	2808	2808	•		67	1.69
14		Y	HDPE	2789	2789	Courting		. 60	1.36
15		Y	HDPE	2820	2820			62	1.41
16		х	HDPE	2890	2890			63	1.40
17		х	HDPE	2890	2890			65	1.67
18		х	HDPE	2840	2840			64	1.51
19		Y	PP	4121	4121 .			109	1.73
20		Y	PP	4140	4140			106	1.75
21		Y	PP	3887	3887			99	1.63
22		х	PP	4200	4200			104	1.75
23		х	PP	4140	4140			103	1.78
24		Х.	PP	4123	4123			110	1.57
25		Y	Acetal	8137	-8137	7451	24	203	3.26
26'	· \	Y	Acetal	8513	8513	7890	59	262	3.67

\*Mean Rate of Stressing.

				Tensi	le Stres	s, psi	Elonga-	*	Modulus
Test #	Medium	Orient- ation	Plastic	Max	Yield	Break	tion at Break %	M.R.S., psi/sec	x 10,5 psi
27	AIR	Y	Acetal	7593	7593	6907	66	¹ <b>1</b> 87	3.47
28		х	Aceta1	8157	8157	7412	32	202	3.54
29		Х.	Acetal	8139	8139	7555	37	202	3.33
30		х	Acetal	8189	8189	7453	32	203	3.29
31		Y	Nylon-11		4250			<b>6</b> 8	1.09
32		Y	Nylon-11		4262	w		74	1.03
33		Y	Nylon-11		4000	****	-	65	1.05
34		Y	PVC	6349	6349	6048	123	224	2.97
35		Y .	PVC	6365	6365	5667	88	213 -	3.60
36		Y	PVC	6278	6278	5706	98	211	3.15
37		х	PVC	6254	6254	5915	114	219	3.17
38		х	PVC	6548	6548	6548	145	223	3.57
39		х	PVC	6365	6365	6143	120	220	3.35
40	S.W.	Y	PP	4607	4607			112	2.17
41		Y	PP	4536	4536			109	2.19
42		Y	PP	4414	4414			106	-2.09
. 43		х	PP	4589	4589			112	2.10
44		Х	PP .	4562	4562	<u>-</u>		111	2.05
45		х	PP	,4570	4570	May 1 mg		110	2.15
46		Y	Acetal	8396	8396	<b>7</b> 849	42	199	3.66
47		Υ .	Acetal	8415	8415	8066	21	202	3.63
48		Y	Acetal	8434	8434	8094	22	202	3.60
49		х	Acetal	8615	8615	8067	26	209	3.35
50		х	Acetal	8731	8731	8308	27	209	3.63
51		х	Acetal	8843	8843	8225	28	214	3.74
52		, Y	CAB	3836	2845	3836	65	93	1.60
L			<u> </u>	ļ	<u> </u>		<u> </u>		

				Tens	ile Stres	s, psi	Elonga-	*	Modulus
Test #	Medium	Orient- ation	Plastic	Max	Yield	Break	tion at Break %	M.R.S., psi/sec	x 10, <sup>-5</sup> psi
53	s.W.	Y	CAB	3789	2886	3789	63	94	1.59
54		Y	CAB	3853	2914	3853	- 65	97	1.64
55		х	CAB	3402	2857	3402	52	94	1.56
56		х	CAB	3571	2902	3571	57	95	1.65
57		х	CAB	3286	2946	3286	50	95	1.66
58		Y	HDPE	2982	2982			68	1.67
59		¥	HDPE	2977	2977	-		69	1.66
60		Y	HDPE	2966	2966		Clinin copes	·67	1.73
61		х	HDPE	3110	3110	avely sarin	····	74 .	1.75
62		x	HDPE	3157	3157			<b>7</b> 5	1.50
63		х	HDPE	3052	3052	epole design		73	1.50
64		Y	PB	2510	2026	2510	42	37	.506
65		Y	PB	2528	2022	2528	38	39	.494
66		Y	PB	2572	2078	2572	45	39	.516
67		х	РВ	2448	2057	2448	30	38	.536
<b>6</b> 8		х	РВ	2474	2015	2474	41	36	.501
69		х	РВ	2454	2031	2454	33	37	.525
70			Nylon-lî		4137			62	. 957
71			Nylon-l'l		4113			61	.950
72			Nylon-l'i		4113			60	.950
73		Y ·	PVC	6948	6948	5690	39	231	3.81
74		Y	PVC	6850	6850			225	3.78
75		Y	PVC	6776	6776			195	3.67
76		х	PVC	6943	6943			231	4.54
77		х	PVC	6778	6778			235	3.38
78	te of Sti	Х	PVC	6694	6694	5435	20	234	3.38

\*Mean Rate of Stressing.

				Tensi	le Stres	s, psi	Elonga-	*	Modulus
Test #	Medium	Orient- ation	Plastic	Max	Yield	Break	tion at Break %	M.R.S., psi/sec	x 10,5 psi
** 79	AIR	Y	HDPE	3655	3655	2111	55	1001	2.31
<b>**</b> 80		Y	PP	5146	5146	4211	16	1205	2.81
** 81		Y	Acetal	9340	9340	9113	20	2473	2.40
** 82		Y	PVC	7864	7864	5091	14	2588	4.60
** 83		Y .	Nylon-11	7115	4705	7115	267	866	1.23
<b>**</b> 84		Y	CAB	4357	3800	4357	40	1124	1.63
** 85		Y	PB	2554	2164	2554	40	375	.520
90	NH <sub>3</sub>	Y	PVC	891	891			7.6	.990
91		Y	PVC	999	881	****		16.9	.980
92		х	PVC	966	935		****	18.5	1.30
93		х	PVC	1056	976		'	19.0	1.40
100		Y	Acetal	7917	6593	7593	75	107	1.69
109	·	Y.	Acetal	8269	7058	8029	63	112	1.58
110		х	Acetal	8132	7075	7877	53	118	1.72
111		Y	Acetal	7864	6964	7864	38	119	1.76
116			Nylon-ll	2873	2690	-		28	.416
117			Nylon-11	2857	2698			29	.402
118		Y	HDPE	2819	2819		<b></b> `	61	1.28
119		Y	HDPE	2902	2902		,	64	1.26
120		x	HDPE	2914	2914	1613	45	65	1.25
121		х	HDPE	2898	2898	1444	57	63	1.14
122		х	РВ	2137	1820	2137	24	25	. 384
123		х	PB	2181	1862	2181	25	26	.379
124		Y	РВ	2348	1804	2348	34	27	.416
125		Y	РВ	2366	1827	2366	33	25	.407
130	<b>V</b>	х	PP	4221	4221			93	1.97
*Moon P	sto of Si	rossina	**Testir		لبيبا	لـــــــــــــــــــــــــــــــــــــ			

\*Mean Rate of Stressing. \*\*Testing speed = 2.0 inches/minute

				Tensi	le Stres	s, psi	Elonga-	*	Modulus
Test #	Medium	Orient- ation	Plastic	Max	Yield	Break	tion at Break	M.R.S., psi/sec	x 10, 5 psi
131	NH 3	Y	PP	4109	4109			90	1.97
132	11	Y	PP	4111	4111			88	1.93
140	C3H8	х	HDPE	2492	2492	686	64	44	-591
141		Y	HDPE	2458	2458			43	.586
142		х	PB	1434	1010	1434	23	22	.303
144		х	Acetal	8510	8510	8178	24	213	3.62
145		X,	Acetal	8316	8316	8012	29	204	3.39
146		Y	PVC ·	6833	6833		_	225	6.08
147		х	PVC	6655	6655		· 	218	3.53
148			CAB	2680	2119	2616	61	70	1.12
149		Y	CAB	2589	2103	2589	59 <sub>.</sub>	70	1.32
150			Nylon-l'I	5027	4488			63	1.02
151			Nylon-l'I	4320	4080	·		57	.88
173	1C, H <sub>10</sub>	х	CAB	3583	2986	3583	50	92	1.37
174	1C4 H10	х	CAB .	4016	3050	4016	52	93	1.41
177	C3 H8	х	PP	3059	3059	2723	78	56	.958
178	C <sub>3</sub> H <sub>8</sub>	х	PP	3270	3270	2832	73	53	-857
179	1C, H1 0		Nylon-11	4766	4297			67	· <b>1.</b> 00
180			Nylon-11	4685	4313			69	1.08
181		х	HDPE	2803	2803			57	.99
182		· x	HDPE	2740	2740	·		55	.923
183		х	Acetal	8712	8712	8239	20	201	3.13
184		х	Acetal	8458	8458	7951	39	204	3.19
185		. <b>x</b>	PVC	7092	7092			218	3.56
186		х	PVC	7039	7039			214	3.30
187		х	PP	2653	2653			38	.614
188		Х.	PP	2773	2773		-	40	.605
*Mean R	ate of St	ressino	<u> </u>	<u> </u>	19				

# CHEMICAL RESISTANCE TEST DATA

# Mechanical Properties after 7 day exposure at 80 F

				Tensi	le Stres	s, psi	Elonga-	*	Modulus
Test #	Medium	Orient- ation	Plastic	Max		Break	tion at Break %	M.R.S., psi/sec	x 10, <sup>-5</sup> psi
189	iC <sub>4</sub> H <sub>10</sub>	х	PB	1845	1363	1845	34	14	.182
190	<b>j</b> )	х	PB	1519	1388	1519	19	13	.174
HDPE-1	Air		HDPE	3089	3089			69.7	1.49
HDPE-2	Air		HDPE	3072	3072	gan tritt valle dans		69.9	1.55
72-1	Air		PDX77372	3193	3193	<del>-,</del>	<b></b>	82.6	1.67
72+2	Air		PDX77372	3494	3494			89.2	2.01
73–1	Air		PDX77373	2938	2938			66.3	1.38
73–2	Air		PDX77373	2759	2759			70.5	1.53
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APPENDIX D

Environmental Rupture Test Data '

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TEST NO.	MEDIUM	PLASTIC	TIME- TO- FAILURE HR.	TEST NO.	MEDIUM	PLASTIC	TIME- TO- FAILURE HR.
1	AIR	HDPE	54.5	24	AIR	PB:	119.8
2			-	25	S.W.	.	1.8
3			743.0	26	AIR	·	0.1
4			616.0	27			5.0
5			1.4	28		·	0.2
6			1.2	29		· .	-
7			8.0	30			2.5
. 8			121.7	31			2.3
9			12.1	32	NH3	HDPE	168.7
10			150.1	33	1		21.3
11		ACETAL	356.2	34			101.8
12			22.5	35			253.4
13			28.4	36			2.8
14			29.2	37			1.2
15			-	38			3.3
16	s.w.		7.5	39			1.3
17	NH <sub>3</sub>		134.8	40			22.5
18	AIR		_	41			-
19			162.6	42			74.0
20			664.8	43	S.W.		4.5
21			344.8	44 .			4.1
22			25.1	45			5.1
23	]	PB.	-	46	¥	Y	1.9

			A 4					TIME
			•	TIME TO-				TIME TO- FAILURE
	EST NO.	MEDIUM	PLASTIC	FAILURE HR	TEST NO.	MEDIUM	PLASTIC	HR
	47	S.W.	HDPE	67.1	70	NH3	PB	0.0
	48		*	3.3	71		•	0.2
	49			3.8	72			32.2
	50			265.1	73	*		0.1
	51		7.0	29.9	74	V		· .
	52			y-	75	AIR		0.2
	53			347.7	76	NH <sub>з</sub>		0.1
	54	NH <sub>3</sub>	ACETAL	-	77			0.0
	55		х .	-	78	4		0.5
	56			0.1	79	S.W.		138.5
	57			-	80	NH <sub>3</sub>		
ļ	58	S.W.		6.8	81			261.5
١	59	X			82			240.2
1	60			- 0	83			1.4
	61	AIR	РВ	695.7	84	AIR		0.8
	62	NH <sub>3</sub>		0.1	85	NH3	V	-
	63	:		0.0	86	S.W.	ACETAL	58.5
	64			0.1	87	NH <sub>3</sub>		-
	65			0.0	88			20.1
	66	S.W.		5.0	89			0.1
	67	S.W.		138.0	90	s.w.		51.9
	68	AIR		0.0	91	NH <sub>3</sub>		64.0
	69	NH <sub>3</sub>	1	0.1	92	1	Ý	9.2

			·		<del></del>	·	·
TEST NO	MEDIUM	PLASTIC	TIME TO- FAILURE HR	TEST NO	MEDIUM	PLASTIC	TIME TO- FAILURE HR
93	NH <sub>3</sub>	ACETAL	2.4	121	AIR	PDX77373	0.0
94	. 1		0.8	122			-
95			0.1	123		PDX77372	0.3
96	S.W.		12.6	124			0.4
97			314.9	125	NH <sub>3</sub>	PDX77373	1.7
98	ı ı		-	126	AIR		11.8
99			357.0	127			18.4
100			1.3	128	NHa	7.0	1.1
101	NH <sub>3</sub>		69.1	129	AIR	PDX77372	3.5
102			33.1	130		PDX77373	3.0
103			61.0	131		PDX77372	4.2
104			25.1	132		PDX77373	4.3
110	AIR	PDX77372	25.7	133	·		1.6
111			4.2	134	J	195, 1	_
112			0.0	135	NH 3		
113			0.4	136			53.8
114			0.0	137			152.5
115	- E X		0.2	138			
116			1.7	139	AIR		1.2
117		PDX77373	-	140			154.9
118	NH <sub>3</sub>	22	5.2	141	NH 3	PDX77372	1.1
119			6.3	142			0.9
120	AIR	¥	0.1	143	V	V	0.2

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TEST NO.	MEDIUM	PLASTIC	TIME TO- FAILURE HR	TEST NO.	MEDIUM	PLASTIC	TIME TO- FAILURE HR
144	AIR	PDX77372	-	167	S.W.	PDX77373	1.9
145			9.4	168			3.2
146			-	169	<b>J</b> -		3.6
147			10.4	170	AIR		908.7
148	NH <sub>3</sub>		0.3	171		. 3	6.5
149			1.5	172			7.2
150			0.3	173	V		218.8
151	S.W.		311.4	174	S.W.		1.7
152			4.2	175	-	- 3	-
153			12.4	176		-	
154			16.3	177	NH <sub>3</sub>	PDX77372	3.4
155			258.5	178			325.1
156			2.9	179	<u> </u>	V	-
157			0.5	180	NH <sub>3</sub>	PDX77372	230.0
158	AIR		25.6	181			6.0
159		Ţ.	-	182			7.3
160	V		-	183			1.3
161	S.W.		0.5	184		- W	0.9
162	AIR	V	18.2	185		-	-
163	S.W.	PDX7737	3 0.1	186	NH 3	PDX77372	1.6
164			17.2	187		PDX77373	2.0
165			60.0	188			0.4
166	Y		0.1	189	The state of the s	-	0.2

			TIME TO- FAILURE				TIME TO- FAILURE
IEST NO.	MEDIUM	PLASTIC	HR	TEST NO.	MEDIUM	PLASTIC	FAILURE HR
190	S.W.	PDX77373	>1000				
191	4		>1000	Å	100		
192	NH <sub>3</sub>		34.4			Ì	
193		- G - C	3.7			(f)	
194			11.6	4	Ye		
195			0.2		,		0
196	,	ō.	530.0				· .
197	s.W.		>1000			7.	*
198			>1000				
205	AIR	F364	0.3		44.		40
206			0.9				E 2.7
207			0.3.	,	•		
208			0.6				
209			7.4		,		
210			4				
211	V		7.2		· · ·		1.45
			.				
	21	Î					
				1			